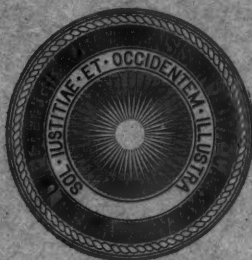


# SOIL SCIENCE

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## SOIL SCIENCE

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# THE INFLUENCE OF VARYING AMOUNTS OF SULFUR IN THE SOIL, ON CROP YIELDS, HYDROGEN-ION CONCENTRATION, LIME REQUIREMENT AND NITRATE FORMATION<sup>1</sup>

J. G. LIPMAN, A. L. PRINCE AND A. W. BLAIR

*New Jersey Agricultural Experiment Station*

Received for publication March 3, 1921

The senior author has already called attention to the rather rapid oxidation of sulfur when intimately mixed with normal soil, and with McLean and Lint (8, 9) has shown that the phosphoric acid of raw rock phosphate, may be made available by means of the sulfuric acid thus formed. He has also suggested the use of a moderate application of sulfur as a means of combating potato scab through the increased acidity of the soil. However, it was recognized that the use of sulfur in this way might have a pronounced prejudicial influence on the soil reaction and also on nitrate formation and crop yields.

In order, therefore, that more definite information might be secured on these points an experiment was planned in which sulfur was used at the following rates per acre in connection with the growing of barley and soybeans, the latter being grown as a second crop without further treatment.

Plot number	Pounds per acre
1a and 1b.....	200
2a and 2b.....	500
3a and 3b.....	1000
4a and 4b.....	2000
5a and 5b.....	4000

Inoculated sulfur was used on the *b* series and uninoculated on the *a*'s.

The plots were approximately square and  $\frac{1}{200}$  acre in area.

All plots received a uniform application of a complete fertilizer analyzing 4 per cent nitrogen, 10 per cent phosphoric acid, and 3 per cent potash, at the rate of 600 pounds per acre. This was made from dried blood, acid phosphate and muriate of potash. Both sulfur and fertilizer were spread broadcast only a few days before barley was seeded on May 3, 1920.

Germination was fairly uniform, but as the season progressed there was very definite indication of injury with the heavier applications of sulfur. This is shown by the dry weights (grain and straw were not separated) reported in table 1. On the uninoculated section (*a*) there is a gradual decline in the

<sup>1</sup> Paper No. 24, of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

yield as the sulfur was increased until with the 4000-pound application the yield is less than half the yield where 200 pounds were used. On the inoculated section the yield was as much with 2000 pounds as with 500 pounds, but with 4000 pounds it was reduced to less than one-half the yield with the 200-pound application. On plots 5a and 5b the blades of the barley plants first turned brown at the tips and then finally died back until at harvest time almost the entire plant was dead. Some weeds and grass grew even after the barley plants had died. The soil of these plots gradually became darker in color than the surrounding soil.

Immediately after the barley was harvested the ground was disked and seeded to soybeans without further sulfur treatment. On plots 1a and 1b germination was about normal, on 2a and 2b not quite so good, on 3a and 3b there were a few scattering plants, and on the remaining plots there was

TABLE 1  
*Dry weights of barley and soybeans from sulfur-treated plots*

PLOT NUMBER	SULFUR APPLIED PER ACRE	BARLEY (GRAIN AND STRAW)	SOYBEAN HAY
Uninoculated section			
	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>
1a	200	2840	968
2a	500	2360	992
3a	1000	2000	690
4a	2000	1710	490
5a	4000	1200	40
Inoculated section			
.1b	200	2460	660
2b	500	2020	826
3b	1000	1730	700
4b	2000	2020	310
5b	4000	1140	32

practically no germination. However, beans which fell around the borders of these plots germinated and grew.

As the season progressed there was considerable growth of crab-grass and weeds on the less acid plots where the stand of beans was incomplete. At the time of harvesting the beans, plots 4a, 4b, 5a and 5b were barren save a few bunches of crab-grass and smart-weed. It was very evident that certain of the weeds and grasses were more resistant to the unfavorable conditions than the soybeans.

The beans were harvested as hay on October 8. The dry weights are reported in table 1 along with the barley weights. It will be noted that the yield was slightly greater in each case with 500 than with 200 pounds of sulfur. This may be due to the fact that the seeding, which was done by hand, was not entirely uniform. Beginning with the 1000-pound application there

is a rather rapid decline in yield until with 4000 pounds of sulfur there were only 32 and 40 pounds, respectively, of dry matter per acre, which consisted of grass and weeds.

#### HYDROGEN-ION CONCENTRATION OF THE SOIL SOLUTION

In order that some information might be gained with reference to the rapidity with which the sulfur was oxidized, it was decided to make hydrogen-ion concentration determinations at intervals of two weeks. Since no check plots were provided in the seeded portion two unseeded plots lying beside the sulfured plots were taken as check plots for the soil work.

TABLE 2  
*Hydrogen-ion concentration expressed as pH values—sulfur-treated plots, 1920*

PLOT NUMBER	MAY 17	JUNE 1	JUNE 14	JUNE 28	JULY 12	JULY 26	AUGUST 9	AUGUST 24	SEPTEMBER 9	SEPTEMBER 23	OCTOBER 7	OCTOBER 21	NOVEMBER 4	NOVEMBER 18	AVERAGE
	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
1, check	5.6	5.6	5.6	5.6	5.7	5.7	5.8	5.9	6.2	6.3	6.2	6.3	6.2	5.9	5.9
2, check	5.8	5.8	5.8	5.8	5.9	5.9	6.0	6.0	6.2	6.4	6.3	6.3	6.2	6.0	6.0
1a	5.8	5.8	5.8	5.8	5.8	5.8	5.9	6.0	6.2	6.1	6.0	6.1	6.1	5.8	5.9
2a	5.6	5.5	5.5	5.7	5.8	5.5	5.6	5.4	5.4	5.8	5.9	5.0*	5.9	5.8	5.6
3a	5.6	5.6	5.5	5.0	4.8	4.8	4.8	4.5	4.6	4.8	4.6	4.9	4.6	4.9	4.9
4a	5.6	5.6	5.6	4.8	4.4	4.0	4.1	4.2	4.0	3.8	3.9	4.0	3.9	3.9	4.4
5a	5.6	5.5	4.9	4.5	3.9	3.9	3.5	3.6	3.8	3.6	3.8	3.8	3.8	3.9	4.2
1b	5.6	5.6	5.6	5.6	5.9	5.8	5.8	5.8	6.1	6.0	6.0	6.1	6.0	5.9	5.8
2b	5.6	5.6	5.6	5.7	5.8	5.8	5.8	5.6	5.8	5.8	5.8	5.9	5.8	6.0	5.8
3b	5.6	5.6	5.6	5.0	4.6	4.7	4.7	4.7	4.7	4.7	4.6	4.4	4.3	4.4	4.8
4b	5.6	5.5	5.4	4.7	4.1	3.9	3.6	3.8	3.9	3.9	3.8	3.8	4.0	4.2	4.3
5b	5.6	5.5	5.0	4.3	3.8	3.9	3.6	3.8	3.8	3.7	3.9	3.9	3.9	3.9	4.2

\* Omitted from average.

Sampling was begun May 17, 2 weeks from the date of seeding the barley. Five or more cores of about 1 inch diameter were taken from each plot, cutting to the depth of  $6\frac{3}{4}$  inches, and these were combined to make one sample for the plot. The samples were immediately taken to the laboratory where they were air-dried and prepared for analysis without grinding. The hydrogen-ion determinations were made by the colorimetric method, the double-tube standard described by Gillespie (5) being used. The results of these determinations are reported in table 2. The check plots ran fairly constant around 5.9 to 6.0 throughout the season, with a slight tendency to become less acid toward the end of the season. Check 1 was slightly more acid than check 2 during the first half of the season. Plots 1a and 1b (200 pounds of sulfur) gave readings quite close to the check plots and here also there was a tendency toward the less acid condition near the end of the season.

On an average 2a shows a slightly higher acidity than 2b, but for a number of the samplings the readings are identical. The point of highest acidity for these plots was reached August 24 (16th week). From this time on, there was a tendency toward a decline in acidity until November 18 when the readings were 5.8 and 6.0, respectively, with an average of 5.6 and 5.8.<sup>2</sup>

Beginning about the sixth to the eighth week plots 3a and 3b (1000 pounds of sulfur) show an increase in acidity. For 3a the maximum acidity occurred

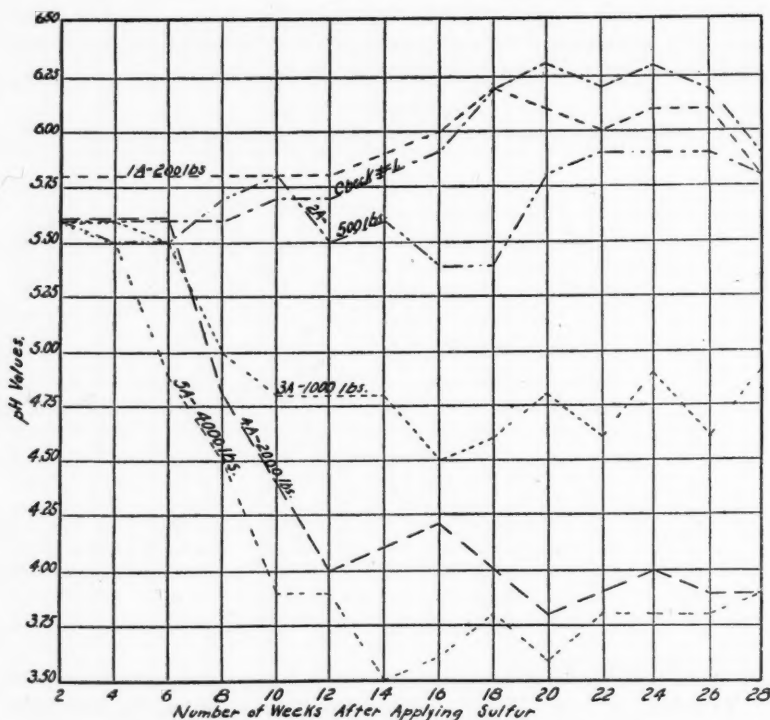


FIG. 1. HYDROGEN-ION CONCENTRATION (pH VALUES) WITH VARYING AMOUNTS OF UNINOCULATED SULFUR

August 24 and for 3b on November 4. The average for the period was 4.9 and 4.8, respectively.

A decided increase in acidity is noted for 4a and 4b on June 28 (eighth week), though 4b showed slight increase the fourth and sixth weeks. The maximum for both plots was reached August 9 when the pH value was 3.6.

<sup>2</sup> A reading of 5.0 for 2a on October 21 has been omitted from the average, since no explanation was found for a reading which differs so widely from those for samples taken two weeks earlier and two weeks later.

On November 18 the readings were 3.9 and 4.2, respectively, with an average of 4.4 and 4.3

The maximum acidity for 5a and 5b also occurred on August 9 when the readings were 3.5 and 3.6, respectively, with a period average of 4.2 and 4.2.

As previously pointed out these plots and also 4a and 4b were so strongly acid that the soybeans were practically a failure.

These differences in reaction are clearly brought out by the graphs in figures 1 and 2.

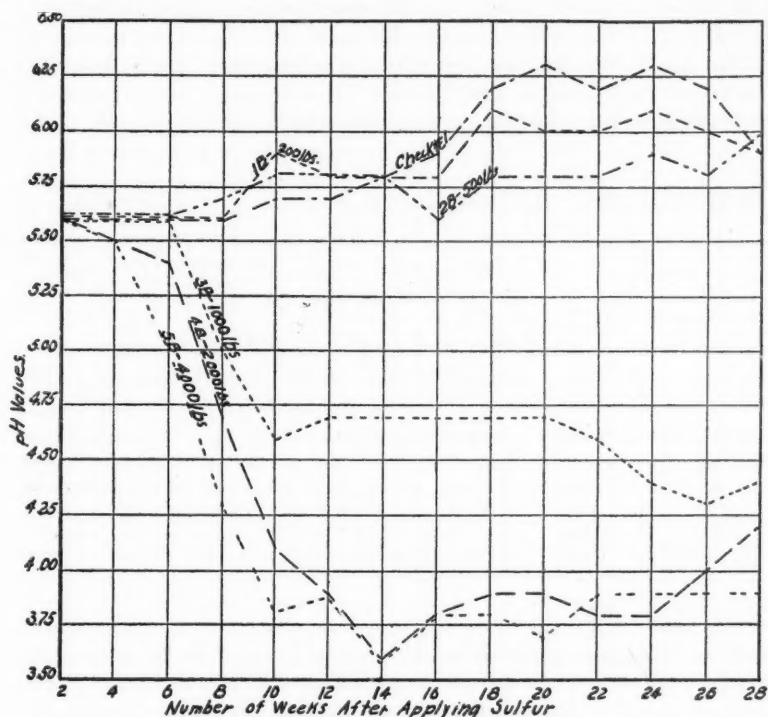


FIG. 2. HYDROGEN-ION CONCENTRATION (pH VALUES) WITH VARYING AMOUNTS OF INOCULATED SULFUR

#### LIME REQUIREMENT COMPARED WITH HYDROGEN-ION CONCENTRATION

Lime-requirement determinations (revised Veitch method) (14) were made on samples from section *a* collected May 17, June 28, August 9, September 23 and November 4, these dates being at intervals of about 6 weeks.

In table 3 these results are compared with the pH values obtained on the same samples. From the table it will be noted that the lime requirement was fairly constant—800 to 1000 pounds—for all of the plots on May 17,



about two weeks from the date of applying sulfur. With only two exceptions (plot 1a) the requirement did not vary greatly from these figures for the check plot and plots 1a and 2a, throughout the season.

On June 28, however, there was a distinct increase beginning with plot 3a (1000 pounds of sulfur per acre), the lime requirement being 1400 pounds. For 4a and 5a the requirement on this date was 2800 pounds.

This rather sharp rise in lime requirement for 3a and 4a is noted again on August 9, September 23 and November 4, and for 5a on August 9, this latter being the highest lime requirement noted during the period under consideration.

It is of especial interest to note that 500 pounds of sulfur did not materially increase the lime requirement over that of the check plot. It did, however, result in some increase in the pH value. In this connection it should be remembered that this land was in crops that were not cultivated. The only

TABLE 3

*Hydrogen-ion concentration and lime requirement of soils from plots that have received different quantities of sulfur*

PLOT NUMBER	SULFUR TREATMENT	MAY 17		JUNE 28		AUGUST 9		SEPTEMBER 23		NOVEMBER 4		AVERAGE	
		pH value	Lime requirement	pH value	Lime requirement	pH value	Lime requirement	pH value	Lime requirement	pH value	Lime requirement	pH value	Lime requirement
1, check	0	5.6	1000	5.6	800	5.8	800	6.3	800	6.2	800	5.90	840
1a	200	5.8	800	5.8	800	5.9	600	6.1	200	6.1	200	5.94	520
2a	500	5.6	800	5.7	600	5.6	1000	5.8	1000	5.9	900	5.70	860
3a	1000	5.6	800	5.0	1400	4.8	2200	4.8	2000	4.6	3000	4.96	1880
4a	2000	5.6	800	4.8	2800	4.1	4600	3.8	6000	3.9	6400	4.44	4120
5a	4000	5.6	1000	4.5	2800	3.5	7600	3.6	6600	3.8	6000	4.20	4800

stirring that it received after the sulfur was harrowed in, was the disking preparatory to seeding the soybeans. Had the land been in cultivated crops it is quite possible that the 500-pound application of sulfur might have influenced the hydrogen-ion concentration and the lime requirement to a greater extent.

Likewise on a different type of soil or with a higher initial pH value the results might have been different.

With soils having, in most cases, a somewhat higher initial pH value than the soil in question, Martin (10) found that 300 to 600 pounds of sulfur per acre did considerably increase the hydrogen-ion concentration of the soil solution as compared with plots that received no sulfur.

The 1000, 2000 and 4000-pound applications of sulfur did make very sharp increases in both the pH values and the lime requirement after the sulfur had been in the ground for about 6 weeks.

The principles involved in the two methods of reporting the soil reaction differ so widely that it is not practicable to attempt a direct comparison. The junior authors (2), however, have already called attention to the fact that an increase in hydrogen-ion concentration, as shown by the pH value, is usually paralleled by some increase in lime requirement.

It is quite evident from the work reported here that a determination of pH values in many cases will enable one to make an approximate forecast of what the lime requirement will be.

For example, in connection with the soils here considered there would seem to be justification for the statement that a pH value of about 5.0 to 4.6 means a lime requirement ranging between 2000 and 3000 pounds. This it must be admitted is a rather wide range, but it may not be much farther out of the way than results secured by some of the methods now in vogue.

The average lime requirement for the five samples of plot 2a is 860, which is practically the same as the average for the check plot. For 3a (1000 pounds of sulfur) it is 1880 pounds, for 4a, 4120 pounds, and for 5a, 4800 pounds. The corresponding pH values are 5.0, 4.4 and 4.2.

#### NITRATE DETERMINATIONS

The samples collected for hydrogen-ion determinations served also for nitrate determinations, which were likewise made at intervals of two weeks. In a consideration of this subject it must be remembered that nitrates are subject to rather wide variations during the season, depending upon several factors, among which may be mentioned rainfall, temperature, the growing crop, the quantity of decomposing organic matter that is present, and possibly in some cases, to soil reaction. Therefore, when the nitrate content becomes less in the presence of a growing crop it is not necessarily an indication that nitrates are not being formed, or are being leached out by percolating rain-water. It may simply mean that they are being utilized by the crop more rapidly than at some other time when a higher concentration was noted.

In determining the nitrates the colorimetric method described by Schreiner and Failyer (12) was used.

As already explained the check plots were not true checks, since no crop was grown on them, nor was any fertilizer used on them. An attempt was made to keep them bare, but at times the weeds and grass made some headway. For these reasons, therefore, the readings obtained from these checks cannot have the value of true checks, but they seem to be of sufficient worth to warrant their inclusion in the report.

Between the fourth and sixteenth weeks there is indication of a considerable accumulation of nitrates on these checks. After this time the concentration is rather low, with the exception of check 2 for the twenty-sixth week (November 4). For all the sulfur-treated plots there is a gradual downward trend in nitrate content until the twelfth week, when the average was less

than one part per million. At this time the check plots gave a reading of 5.6 and 4.0 parts of nitrates per million.

The rainfall at the New Jersey station for the months of June, July and August, 1920, was above the last preceding 10-year average for these months, and it might be claimed that the low nitrate content on the sulfur-treated plots during this period was due to the leaching out of the nitrates by percolating rain-water. Such a claim, however, does not seem logical in view of the rather high content of nitrates found on the check plots during these months. These received no nitrogenous fertilizer, and certainly if the depres-

TABLE 4  
*Nitrates (NO<sub>3</sub>) expressed as parts per million in sulfur-treated plots, 1920*

PLOT NUMBER	MAY 17	JUNE 1	JUNE 14	JUNE 28	JULY 12	JULY 26	AUGUST 9	AUGUST 24	SEPTEMBER 9	SEPTEMBER 23	OCTOBER 7	OCTOBER 21	NOVEMBER 4	NOVEMBER 18	AVERAGE
1, check	3.7	7.5	5.8	17.7	11.1	5.6	14.9	10.2	2.3	1.4	1.5	2.0	1.4	2.6	6.3
2, check	3.0	3.7	5.9	9.2	11.9	4.0	8.8	4.4	1.5	1.3	1.8	2.1	14.1	1.8	5.3
1a	10.8	4.6	1.2	2.0	1.2	1.1	2.2	1.9	1.2	1.3	0.9	1.2	1.3	2.1	2.4
2a	3.8	3.5	1.2	1.8	1.2	1.0	3.5	1.8	1.4	1.5	1.2	1.1	1.5	4.4	2.1
3a	3.5	4.1	1.0	1.6	1.1	0.8	2.3	2.1	2.6	4.0	3.3	4.7	2.4	5.3	2.8
4a	4.1	2.4	1.1	1.2	1.0	0.9	1.2	1.8	5.8	4.4	4.0	5.9	4.0	6.6	3.2
5a	6.2	3.4	0.9	1.1	1.2	0.8	2.0	1.8	4.2	4.0	4.4	4.2	4.4	4.4	3.1
Average 1a-5a.....	5.7	3.6	1.1	1.5	1.1	0.9	2.2	1.9	3.0	3.0	3.0	3.4	2.7	4.6	
1b	4.7	1.8	1.1	1.5	1.1	0.9	3.3	1.5	1.4	1.2	1.2	1.5	1.6	2.2	1.8
2b	3.4	1.9	1.1	1.6	1.1	0.8	2.9	1.9	1.0	1.6	1.5	1.6	2.4	2.2	1.7
3b	2.5	1.8	0.8	1.1	0.9	0.7	3.3	1.8	2.4	2.1	3.0	2.2	1.9	3.9	2.1
4b	4.6	1.9	1.3	1.1	0.9	0.8	1.8	1.3	2.7	4.4	4.4	2.7	7.3	8.8	3.2
5b	4.7	2.8	1.3	1.2	0.9	1.0	1.8	2.1	2.9	5.1	3.1	3.7	16.4*	2.2	2.3
Average 1b-5b.....	4.0	2.0	1.1	1.3	1.0	0.8	2.6	1.7	2.1	3.0	2.6	2.3	3.3	4.0	

\* Omitted from average.

sion had been caused by the leaching out of the nitrates these plots should have shown at least as low a concentration as the sulfur-treated plots which did receive a nitrogenous fertilizer.

It seems evident, therefore, that the low nitrate concentration noted on the sulfur-treated plots during July and August must be attributed to the removal of nitrates by the growing crop, for the barley (and weeds which were mixed with it), did make a fair growth on plots 1 to 3 of each section and some growth on plots 4 and 5. It is of interest to note that the low point in this downward trend of nitrate concentration was reached near the time of harvesting the barley. From July 26, when the average concentration of the treated plots

was less than one part per million, to August 9, there was a distinct increase in nitrates for all plots, including the checks. This would seem to indicate a period of rather rapid nitrification, but the increase was no doubt due in part to the fact that the soybeans (and weeds which grew with them) had not yet made very much growth.

From August 9 to 24 there was a decrease in nitrate concentration on nearly all the plots, the average at this time being less than two parts per million. From August 24 to November 4, plots 1 and 2 of each section showed a fairly uniform concentration, the amount varying between one and two parts per million. During this same period plots 3 to 5, inclusive, on both sections showed a distinctly higher concentration. This higher concentration was well maintained until the last sampling on November 18, at which time the work was stopped on account of the difficulty of securing samples during freezing weather.

This increase of nitrates on the plots that received from 1000 to 4000 pounds of sulfur per acre was no doubt due to the fact that they were supporting very little plant growth during this period.

This gradual increase of nitrate formation under such acid conditions would seem to indicate that nitrification was not seriously hindered on account of the rather extreme acid condition of the soil.

This is contrary to the generally accepted opinion and also to results secured by Hall and his associates (6), who found that nitrification was much hindered on permanent grass lands which were highly acid.

On the other hand, it is in accord with results secured at the Pennsylvania station where Brown and MacIntire (3) and later White (15) showed that frequently nitrification proceeded as rapidly on soils having a high lime requirement as on those having a low requirement.

It is further corroborated by results secured by the junior authors (unpublished data) during the summer of 1920. Nitrate determinations were made at intervals of two weeks beginning May 29 and continuing until November 25 on samples from field plot 11A, which has received annual dressings of ammonium sulfate without lime since 1908, and now has a lime requirement of 2500 to 3000 pounds of CaO for the plowed acre, and from field plot 11B which receives the same ammonium-sulfate treatment, but is limed at intervals of 5 years and is now about neutral in reaction.

The former gave an average of 16.22 parts of nitrate per million with a range of 1.11 parts on August 9 and 46 parts on June 28, and the latter an average of 6.29 parts per million and a range of 2.21 parts on June 14 and 17.68 parts on May 29. In this connection it must be explained that plot 11B yielded a much larger crop than 11A, and therefore utilized more of the soil nitrates, but at the same time it is evident that nitrification was proceeding freely, for the rainfall during the period was above normal.

Fraps (4) studied the nitrifying power of acid and non-acid soils, and found that some acid soils showed high nitrifying power, while others showed a low

nitrifying power. The work was carried out on 500 gm. of soil in percolators. He concluded that "acid soils nitrify slightly less, on an average, than non-acid soils with a low lime content. Some acid soils do not nitrify at all, or have a low nitrification, while other acid soils have a high nitrification."

Noyes and Conner (11) made nitrification studies on five typical acid soils and concluded that "the amount of nitrates present and the nitrifying power of the untreated acid soils varied with the organic matter and total nitrogen rather than with the soil acidity."

Hoagland (7) found as high as 100 to 3000 parts per million of nitrates (dry-soil basis) in peat soils which gave pH values as low as 6.0 to 4.5.

Temple (13) added 1 gm. of tartaric acid, or its equivalent of citric acid, along with ammonium tartrate, to 200 gm. of soil and found that while the amount of nitrites and nitrates formed was not as large as in soils to which ammonium tartrate and calcium carbonate had been added, the amount formed was decided.

Ames and Richmond (1) found that the oxidation of sulfur in soils not well supplied with bases, resulted in depressing the activities of nitrifying organisms.

#### SUMMARY

Barley and soybeans (residual crop) were grown on plots to which inoculated and uninoculated sulfur had been applied at the rate of 200, 500, 1000, 2000 and 4000 pounds per acre.

The barley showed fair germination on all the plots, but as the season progressed there was evidence of injury with 1000 pounds and over of sulfur. Before harvest the plants on the plots that received 4000 pounds of sulfur had practically all been killed.

With 200 and 500 pounds of sulfur germination and growth of the soybeans appeared to be about normal. With 1000 pounds and over germination was very materially depressed, there being very few plants on the plots that received 2000 and 4000 pounds of sulfur.

Determinations of hydrogen-ion concentration and nitrates were made on samples of soil from all plots collected at intervals of about two weeks beginning May 17 and continuing until November 18.

Applications of 200 and 500 pounds of sulfur did not very materially change the hydrogen-ion concentration throughout the season. Applications of 1000 to 4000 pounds caused a decided increase in concentration after the fourth to eighth weeks. In most cases the highest concentration was reached toward the last of July or early in August. The minimum pH value noted was 3.5 on plot 5a, and 3.6 on plot 5b, both of these readings being obtained August 9.

Lime-requirement determinations were made on a limited number of the samples collected at intervals of about 6 weeks. From data thus obtained it was found that the 200 and 500-pound applications of sulfur did not materially influence the lime requirement; the heavier applications did cause very decided increases in lime requirement. It was noted that in most cases an



increase in hydrogen-ion concentration was accompanied by an increase in lime requirement, but there is not a direct correlation. The work seems to indicate the possibility of an approximate forecasting of lime requirement from the hydrogen-ion concentration, though the relationship differs with different soils and under different treatments.

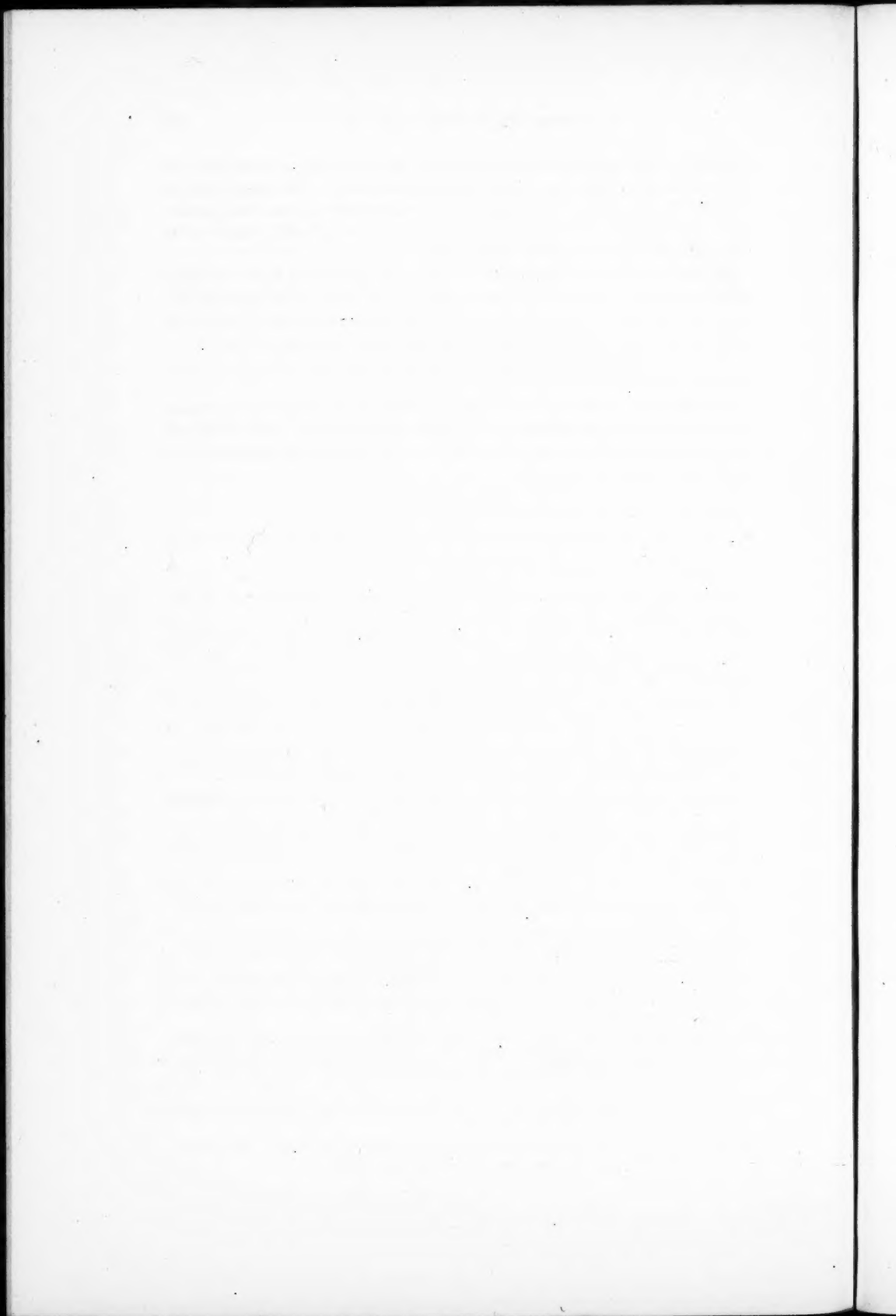
The nitrates varied rather widely, apparently depending upon the crop growth. On an average they were higher on the check plots than on the treated plots, but in this connection it must be remembered that these check plots did not grow a crop, but were kept nearly free from vegetation.

The lowest concentration of nitrates was noted near the end of July, soon after the barley had been harvested.

Nitrates were found in considerable quantities in samples from those plots that showed the highest hydrogen-ion concentration. This seems to indicate rather definitely that nitrification is not necessarily inhibited by a highly acid condition of the soil.

#### REFERENCES

- (1) AMES, J. W., AND RICHMOND, T. E. 1918 Sulfonation in relation to nitrogen transformations. *In* Soil Sci., v. 5, no. 4, p. 311-321.
- (2) BLAIR, A. W., AND PRINCE, A. L. 1920 The lime requirement of soils according to the Veitch method, compared with the hydrogen-ion concentration of the soil extract. *In* Soil Sci., v. 9, no. 4, p. 253-259.
- (3) BROWN, B. E., AND MACINTIRE, W. H. 1910 Seasonal nitrification and soil moisture in four plats treated with commercial fertilizers. *In* Pa. State Coll. Agr. Exp. Sta. Ann. Rpt., 1909-10, pt. 2, p. 50-57.
- (4) FRAPS, G. S. 1920 Nitrification in Texas soils. *Tex. Agr. Exp. Sta. Bul.* 259.
- (5) GILLESPIE, LOUIS J. 1920 Colorimetric determinations of hydrogen-ion concentration without buffer mixtures, with especial reference to soils. *In* Soil Sci., v. 9, no. 2, p. 115-136.
- (6) HALL, A. D., MILLER, N. H. J., AND GIMINGHAM, C. T. 1908 Nitrification in acid soils. *In* Proc. Roy. Soc. London, s. 3, v. 80, no. B539, p. 196-212.
- (7) HOAGLAND, D. R. 1918 The relation of the plant to the reaction of the nutrient solution. *In* Science, *n.s.*, v. 48, no. 1243, p. 422-425.
- (8) LIPMAN, J. G., MCLEAN, H. C., AND LINT, H. CLAY. 1916 The oxidation of sulfur in soils as a means of increasing the availability of mineral phosphates. *In* Soil Sci., v. 1, no. 6, p. 533-539.
- (9) LIPMAN, J. G., MCLEAN, H. C., AND LINT H. CLAY 1916 Sulfur oxidation in soils and its effect on the availability of mineral phosphates. *In* Soil Sci., v. 2, p. 499-538.
- (10) MARTIN, WILLIAM H. 1920 The relation of sulfur to soil acidity and to the control of potato scab. *In* Soil Sci., v. 9, no. 6, p. 393-408.
- (11) NOYES, H. A., AND CONNER, S. D. 1919 Nitrates, nitrification and bacterial contents of five typical acid soils as affected by lime, fertilizers, crops, and moisture. *In* Jour. Agr. Res., v. 16, no. 2, p. 27-42.
- (12) SCHREINER, OSWALD, AND FAIRYER, G. H. 1906 Colorimetric, turbidity and titration methods used in soil investigations. U. S. Dept. Agr. Bur. Soils Bul. 31.
- (13) TEMPLE, J. C. 1914 Nitrification in acid or non-basic soil. *Ga. Agr. Exp. Sta. Bul.* 103.
- (14) VEITCH, F. P. 1920 Report on the lime requirement of soils. *In* Jour. Assoc. Off. Agr. Chem., v. 3, no. 3, p. 371-374.
- (15) WHITE, J. W. 1914 Nitrification in relation to the reaction of the soil. *In* Pa. State Col. Agr. Exp. Sta. Ann. Rpt., 1913-14, pt. 2, p. 70-80.



## METHODS OF STUDYING THE CONCENTRATION AND COMPOSITION OF THE SOIL SOLUTION<sup>1</sup>

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A more exact knowledge of the soil solution is desirable for the study of many of the problems of soil fertility and related subjects. The purpose of the present investigation was to study some of the methods which have been used in determining the concentration and composition of the soil solution and to compare the results obtained by the different methods.

The methods which have been used may be classified into groups as follows:

(a) Methods involving extraction with comparatively large amounts of water.

(b) Methods which aim to obtain the true soil solution.

(c) Methods which aim to measure the concentration of the soil solution directly in the soil.

The water-extraction method has been widely used and possesses many advantages. The greatest criticism of the method is that the addition of a large quantity of water alters the equilibrium in the soil. It undoubtedly has a solvent effect and may also cause a precipitation of some of the material in solution due to an alteration in the nature of the solvent. The quantity of salts obtained depends upon a number of factors. Mitscherlich (17) has shown the effect of the CO<sub>2</sub> content of the water, the time of extraction, and the ratio of soil to water on the quantity of material extracted. The procedure is arbitrary, but results obtained by several investigators indicate that the usual 1:5 extraction gives an approximate measure of the salt content of the soil solution.

Because of the lack of knowledge as to whether or not the water extraction gives a good quantitative measurement of the salts in the soil, there have been several methods proposed for obtaining the true soil solution.

Ramann, Marz and Bauer (21) have obtained the soil solution by the use of a hydraulic press. They applied a pressure of about 4,000 pounds to the square inch. Lipman (16) also used the pressure method, applying a maxi-

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mum pressure of 53,000 pounds to the square inch. The method is of limited value for it is only applicable to finer-textured soils at a rather high moisture content and requires a complicated apparatus. The criticism has been made by Northrup (19) that the application of high pressures such as were used by Lipman would alter the physico-chemical equilibrium in the soil and as a result the true soil solution would not be secured.

The centrifuge method of Briggs and McLane (23) and the artificial root method of Briggs and McCall (8), in which suction is used, may give the true soil solution. However, these methods are only applicable to soils at high moisture contents and only small amounts of the solution are obtained.

The displacement method was first used by Schloesing (22). He used water colored with carmine to displace the soil solution and obtained considerable amounts which were used for analytical purposes. Gola (9) used water as the displacing liquid in his studies on the concentration of the soil solution. Ischerekov (15) used ethyl alcohol as the displacing liquid and obtained results which indicate that the displaced solution is the true soil solution in an unaltered condition. Moist soil was packed in a glass tube which had a piece of linen tied over the bottom. After placing alcohol on top of the soil column the soil solution soon began to drop from the bottom of the tube. He reports results which indicate that the successive portions of the displaced solution are of the same composition, and that the concentration of the soil solution is inversely proportional to the moisture content of the soil.

Van Suchtelen (25) modified Ischerekov's method by using paraffin oil as the displacing liquid and applying suction to hasten displacement. Morgan (18) used a combination of the pressure and displacement methods in which a heavy oil was used as the displacing liquid and applied pressures of about 500 pounds to the square inch to force the oil into the packed soil. Large quantities of the soil solution were thus obtained. The method is open to the objection that it requires a complicated apparatus and the use of a heavy oil makes it uncleanly.

The writer has been unable to find any reference in the literature in which a comparison was made of the results obtained by the displacement and water-extraction methods.

Several methods have been suggested for determining the concentration of the soil solution directly in the soil. Among the first of these was the measurement of the salt content by electrical conductance (10). The method is of some use in determinations of alkali in soils but the results are affected by the texture, organic matter, carbonates, and the moisture content of the soil. It has not proved of any great value in investigational work.

Bouyoucos and McCool (5, 6) have advanced the freezing-point method as a means of determining the concentration of the soil solution directly in the soil, and as a means of measuring the absolute salt content of the soil (7). The results obtained by this method will be discussed in the latter portion of this paper.

In the present investigation a study was made of the displacement and freezing-point methods. The results obtained by displacement are compared with those obtained by the freezing-point and water-extraction methods.

#### THE DISPLACEMENT METHOD

##### *Description of the method and procedure*

The method consists of packing the moist soil in a cylinder provided with an outlet at the bottom. The displacing liquid is then poured on top of the soil column and as it penetrates the soil it displaces some of the soil solution which forms a zone of saturation below the displacing liquid. This zone increases in depth as it is continually forced downward by the pressure of the liquid above. When the saturated zone reaches the bottom of the soil column the clear soil solution, free of alcohol, drops from the soil as gravitational water.

The only apparatus required is a cylinder in which to pack the soil. The diameter of the soil column very largely determines the rate at which the soil solution will be obtained. The height of the soil column likewise determines the time required for displacement. These two factors must be considered in the selection of the cylinder to be used.

Three different-sized cylinders were used in the present investigation. Brass soil tubes 2 inches in diameter and 9 or 12 inches in depth were used in the preliminary work and when only small amounts of the soil solution were desired. Large brass soil tubes 3 inches in diameter were used for securing larger quantities of the solution and in studying the composition of successive portions of the displaced solution. These tubes were made in 6-inch sections and three or four sections were generally used. The bottom section was provided with a false screen bottom and a small outlet. Glass percolators, 2 $\frac{3}{4}$  inches in diameter at the top and 15 inches deep, were used in most of the work. The bottom of the percolator was fitted with a small one-hole stopper. A small quantity of coarse quartz sand was placed in the percolator before adding the soil.

The soil was packed in the tubes by means of a short wooden rod. No difficulty was experienced in obtaining uniform packing. The degree of packing is determined by the kind of soil and its moisture content. Sandy soils were packed as firmly as possible at all moisture contents. Peats also may be packed firmly, for there is no danger of puddling the soil and rendering it impervious to the displacing liquid. With the heavier classes of soil care must be taken to prevent puddling during the packing, in which case the rate of displacement is exceedingly slow or entirely prevented. For this reason it is best to use the heavier soils at a moisture content somewhat below the optimum for plant growth. Under proper moisture conditions the soil should not stick together too readily when squeezed in the hand but should be rather granular and easily worked. Miami silt loam was best used at a moisture



content of about 20 per cent and when properly packed had an apparent specific gravity of 1.50 to 1.60. After a little experience one can readily determine the proper degree of packing for any soil at a given moisture content.

After packing, the cylinders were placed in ring stands and the displacing liquid added and maintained at a depth of 2 to 3 inches.

The time required for displacement varied widely, depending on the moisture content of the soil, the degree of packing, the soil type and the height of the soil column. In most cases it is possible to complete the displacement in 12 hours if the height of the soil column is not over 12 or 14 inches. The displacement may be stopped at any time by removing the layer of the displacing liquid on top of the soil column. In some cases the displacement was started in the evening and completed the next day. When silt loam soils were very firmly packed it sometimes required several days to complete the displacement.

In the water-extraction method the extracts were made by adding the desired amount of distilled water to the soil in a large mortar and stirring for 3 minutes. After settling 12 minutes the suspension was filtered through Pasteur-Chamberland filters.

In the displacement method filtration is unnecessary and total salts were determined by evaporating 25 cc. of the soil solution in a platinum crucible. In the water-extraction method larger quantities were evaporated in platinum dishes. After evaporation the crucibles and dishes were placed in an electric oven at 105°C. for 12 hours. The weight of the residue represented total salts before ignition. The crucible and contents were then ignited to constant weight to determine the total salts after ignition.

Nitrates were determined colorimetrically by the phenoldisulfonic acid method.

Calcium was determined volumetrically by titration of the oxalate with potassium permanganate.

Freezing-point determinations were made in the usual manner with a Beckman thermometer.

#### *The effect of different displacing liquids on the time and percentage displacement*

Water, ethyl alcohol, and paraffin oil were the liquids employed by previous investigators who used the displacement method. It seemed desirable to try other liquids to determine which would give the most complete and rapid displacement. In the preliminary work it was found that liquids which were non-miscible with water such as benzene, kerosene, ligroin, and ethyl acetate would not satisfactorily displace the soil solution. These liquids passed through the soil in practically an unaltered condition and displaced practically none of the soil solution. To use these liquids it would be necessary to pack the soil more and use pressure, as was done by Morgan (18).

The four liquids studied were ethyl alcohol, methyl alcohol, acetone and water. Miami silt loam at a moisture content of 21 per cent was packed in

four 3-inch brass cylinders, care being taken to obtain uniform packing. The degree of packing in these cylinders was not great enough to obtain the most complete displacement. The time which elapsed between the addition of the displacing liquid and the appearance of the first drop of the soil solution was recorded. The volume of the water in the soil being known, the percentage displaced was readily calculated from the volume of the solution obtained. In order to detect the first appearance of the displacing liquid in the soil solution a freezing-point determination was used. The freezing point of successive portions of the solution was determined. As soon as the displacing liquid appeared in the solution the freezing point was appreciably changed. The appearance of ethyl alcohol and acetone was further confirmed by qualitative tests.

Table 1 shows the effect of different liquids on the time and percentage displacement. The viscosity of the liquids also is given in the table, since viscosity is one of the main factors influencing the time and percentage displacement. The less viscous displacing liquids pass through the pore spaces of

TABLE 1

*The time and percentage displacement of the soil solution from Miami silt loam by different liquids*

DISPLACING LIQUID	VISCOSITY IN C. G. S. UNITS AT 20°C.	TIME TO THE FIRST DROP	DISPLACEMENT
		hrs.	per cent
Acetone.....	0.00334	2	12.0
Methyl alcohol.....	0.00591	3½	24.0
Water.....	0.01006	4	20.0
Ethyl alcohol.....	0.01190	4½	36.0

the soil more readily than do the more viscous liquids. This causes them to mix with a greater portion of the soil solution.

These and similar results obtained with other soils indicate that ethyl alcohol is the most satisfactory displacing liquid. It gives a more complete displacement than the other liquids used and it is very easy to test for its appearance in the displaced solution by means of the iodoform reaction.

Water is a fairly satisfactory displacing liquid but it mixes more with the soil solution and does not give as complete a displacement as does ethyl alcohol. If water is used some NaCl should be added making it possible to determine when the displacing solution appears by testing with silver nitrate.

Acetone is not at all satisfactory for it has too low a viscosity and therefore passes through the soil too readily, giving a very low percentage displacement. Methyl alcohol possesses no marked advantage over water and is not as good as ethyl alcohol.

Before ethyl alcohol was selected for subsequent work, additional experiments were made to determine the percentage displacement that would ordinarily be obtained by its use. The percentage displacement depends upon

several factors. The higher the soil column and the more compact the soil, the greater will be the percentage of the soil solution displaced. A high moisture content also tends to produce a high percentage displacement. However, these same factors determine very largely the time required for displacement, and the time element should not be made too great.

The experiments indicated that it was practicable with most soils to obtain from 35 to 45 per cent of the soil solution by displacement with ethyl alcohol. This amount may be secured without the time element becoming very objectionable. It is possible to displace a much greater percentage than this. Using a silt loam soil at a moisture content of 23.3 per cent, a 75.6 per cent displacement was secured. Ischerekov (15) reports that with a soil at saturation it is possible to displace 95 per cent of the soil solution.

*The concentration of the soil solution obtained by the use of different displacing liquids*

A consideration of the mechanics of displacement leads to the conclusion that the soil solution obtained is in all cases really displaced by the soil solu-

TABLE 2  
*The concentration of the soil solution obtained with different displacing liquids*

DISPLACING LIQUID	TOTAL SALTS IN SOLUTION		FREEZING-POINT DEPRESSION OF SOLUTION
	Before ignition	After ignition	
	<i>p. p. m.</i>	<i>p. p. m.</i>	°C.
Acetone.....	655	248	0.020
Methyl alcohol.....	649	246	0.019
Water.....	670	232	0.020
Ethyl alcohol.....	660	248	0.019

tion itself. A zone, in which the soil is saturated with the soil solution, soon forms immediately below the displacing liquid after it is added. After the formation of this zone the only function of the displacing liquid is to give pressure and cause a downward movement of the saturated zone. Therefore, the displacing liquid should not affect the concentration of the solution obtained. The question of the influence of the displacing liquid on the concentration of the solution was studied experimentally, using the solutions secured from Miami silt loam by the different liquids shown in table 1. The results are recorded in table 2 and confirm the conclusions reached by a theoretical consideration of the question.

*Composition of successive portions of the displaced solution*

In displacement the soil solution moves through the soil. The first portions move only a short distance before they drop from the soil, while the last portion may pass through a soil column of considerable height. The question

at once arises as to whether or not the movement of the soil solution through the soil alters its composition. If it does, successive portions of the displaced solution would not be of the same composition. If they are not of the same composition the method probably would be of little value.

In a well mixed soil the solution in all portions is probably of the same composition. The readily soluble salts are in solution and this solution is in equilibrium with the surrounding solid material. As the solution is displaced and passes downward it comes in contact with more solution of the same composition and concentration and with solid material of the same nature as that from which it was displaced. Therefore, the point of equilibrium should not change and the composition of the solution should not be altered by its pas-

TABLE 3

*The freezing-point depression and total salts in successive portions of the soil solution from Miami silt loam*

PORTION	FREEZING-POINT DEPRESSION	TOTAL SALTS IN SOLUTION	
		Before ignition	After ignition
	°C.	<i>p. p. m.</i>	<i>p. p. m.</i>
1	0.024	480*	200*
2	0.023		
3	0.024	352	168
4	0.025		
5	0.024	360	176
6	0.022		
7	0.022	324	172
8	0.025		
9	0.076†	344	180
10	0.098†		
11	0.163†	344	176
12	0.309†		
13	0.444†	496*	256*
14	0.689†		

\* High results due to colloidal material.

† High results due to alcohol in the solution.

sage through a column of soil which has been well mixed before it is packed in the cylinder. Hoagland, Martin and Stewart (14) have shown that a water extract of a soil when concentrated and allowed to percolate through another portion of the same soil does not alter much in its composition. It is therefore probable that the composition of the true soil solution would not be changed in passing through a soil column.

If the soil solution has a solvent effect on the soil particles during its passage through the soil, the last portions would be more concentrated than the first. To determine whether or not successive portions are of the same composition, as indicated by a determination of the freezing point and total salts, a 3-inch brass cylinder was filled with Miami silt loam containing 22 per cent moisture.

The height of the soil column was 22 inches and 35.3 per cent of the soil solution was obtained. During displacement, successive portions were secured and the freezing point determined. Then portions 1 and 2, 3 and 4, 5 and 6, etc., were combined and the total salts determined in these larger portions. Table 3 presents the results.

The first portion contained a small amount of colloidal material which caused a high result for total salts in that portion. Small amounts of alcohol began to come through in the ninth portion, as is indicated by the freezing-point depression. However, the amount was so small that the total salts were not affected until the thirteenth portion. Then the solution became turbid due to colloidal material.

The results show that successive portions are of the same composition. Results have also been obtained showing that successive portions contain the same amount of nitrate nitrogen. It is probable that a complete analysis of the successive portions would prove that they were of the same composition in all respects. These results agree with those obtained by Ischerekov (15) and Schloesing (22). Ischerekov determined total salts and Schloesing determined nitrates.

#### *The concentration of the soil solution at different moisture contents*

In most soils the soil solution is very dilute. All readily soluble material is in solution even at low moisture contents. The solution is only saturated in respect to those minerals which are comparatively insoluble and have a low rate of solubility. Therefore, the addition of a small amount of water should not bring a very appreciable amount of material in solution. That soils are very insoluble and have a low rate of solubility has been shown by the work of Bouyoucos (2), in using the freezing-point method. That being the case, the concentration of the soil solution should be approximately inversely proportional to the moisture content of the soil. The displacement method is well adapted to such a study, for it can be used at a wide range of moisture contents. If the concentration of the soil solution obtained from a soil at different moisture contents is inversely proportional to the moisture content, it affords further proof that the method gives the true soil solution.

The relation of the moisture content and the concentration of the soil solution was studied in three soils. The soils had been in the greenhouse in a moist condition several weeks. Portions of the moist soil were weighed out; to some portions water was added to give the desired moisture content while others were allowed to dry to lower the moisture contents. Before packing in the percolators all portions except those at the higher moisture contents were passed through a coarse screen to insure thorough mixing. Displacement was started as soon after the addition of water as possible, usually within 4 to 6 hours.

Tables 4, 5 and 6 give the results obtained with Plainfield sand, Miami silt loam and Carrington silt loam. If the concentration is inversely propor-



tional to the moisture content, the freezing-point depression of the solution multiplied by the moisture content of the soil will give a constant ( $D:M = K$ ). Also the parts per million of total salts in the dry soil will be a constant.

TABLE 4

*The freezing-point depression of the soil solution and the total salts in Plainfield sand at varying moisture contents*

MOISTURE CONTENT	FREEZING-POINT DEPRESSION OF SOLUTION	$K (D.M=K)$	TOTAL SALTS IN SOIL	
			Before ignition	After ignition
<i>per cent</i>	<i>°C.</i>		<i>p. p. m.</i>	<i>p. p. m.</i>
4.25	0.045	0.191	62	13.1
6.31	0.030	0.189	45	13.7
8.30	0.022	0.182	57	12.9
10.70	0.018	0.192	50	14.7
12.40	0.014	0.173	49	14.1
15.00	0.013	0.195	54	15.1

TABLE 5

*The freezing-point depression of the soil solution and the total salts in Miami silt loam at varying moisture contents*

MOISTURE CONTENT	FREEZING-POINT DEPRESSION OF SOLUTION	$K (D.M=K)$	TOTAL SALTS IN SOIL	
			Before ignition	After ignition
<i>per cent</i>	<i>°C.</i>		<i>p. p. m.</i>	<i>p. p. m.</i>
10.30	0.039	0.401	116.8	44.4
13.55	0.030	0.406	116.1	47.1
17.25	0.022	0.379—	104.3	43.4
20.62	0.018	0.371	108.9	44.8
29.41	0.013	0.382		
34.05	0.012	0.408		

TABLE 6

*The freezing-point depression of the soil solution and the total salts in Carrington silt loam at varying moisture contents*

MOISTURE CONTENT	FREEZING-POINT DEPRESSION OF SOLUTION	$K (M.D=K)$	TOTAL SALTS IN SOIL	
			Before ignition	After ignition
<i>per cent</i>	<i>°C.</i>		<i>p. p. m.</i>	<i>p. p. m.</i>
8.77	0.100	0.877	275	94.0
11.80	0.071	0.837	253	92.3
13.95	0.067	0.934	253	94.2
16.00	0.045	0.720	252	95.3
18.55	0.043	0.797	253	96.0

The results show that within experimental error  $K$  and the parts per million of total salts are constants. Assuming that the concentration of the soil solution is inversely proportional to the moisture content, as is undoubt-

edly very nearly the case, these results indicate that the true soil solution is obtained. Ischerekov (15) preformed a similar experiment and obtained results of the same order.

*A comparison of results obtained by displacement and water extraction*

In a study of any method it is desirable to compare results obtained by its use with those obtained by other methods. The water extraction method is the one most generally used in studying the soluble salt content of soils. It was therefore used as a means of further studying the results obtained by the displacement method. The two methods can not be expected to give the same results in all cases but the result should be of the same general order.

All nitrates are readily soluble and undoubtedly a very nearly correct quantitative determination of the nitrate nitrogen in the soil solution is

TABLE 7  
*Nitrate nitrogen in the dry soil as determined by the water-extraction and displacement methods*

SOIL NUMBER	NITRATE NITROGEN IN THE DRY SOIL	
	Displacement method	Water extraction
	<i>p. p. m.</i>	<i>p. p. m.</i>
1	4.5	4.0
2	54.6	52.0
3	31.0	34.0
4	103.3	100.0
5	53.2	50.0
6	63.3	60.0
7	17.3	20.0
8	38.0	36.0
9	2.4	2.8
10	6.9	6.4

secured by the usual 1.5 water extraction. Since all of the nitrates are probably in the soil solution before the addition of water, it should be possible to obtain the same results for nitrates in the soil by using the two methods. The results obtained with the two methods on a number of soils from different field plots and the greenhouse are given in table 7.

The two methods, within experimental error, give the same result for nitrate nitrogen in the soils. We may therefore conclude that the displaced solution is of the same nitrate concentration as the solution in the soil. It is also evident that the solution is of the same concentration as the soil solution remaining in the soil. If this were not the case the results for nitrates would not agree. Probably the only difference between the displaced solution and the same solution as it existed in the soil, is that when in the soil it was under the influence of a physical force, adhesion, which held it to the soil particles.

A further comparison of the two methods was made by using Miami and Carrington silt loam and determining the total salts and calcium. The water-

extraction method cannot be expected to give exactly the same results for total salts and calcium as the displacement method, since the addition of a very large amount of water undoubtedly affects to some extent the amount of material in solution. As several investigators (17, 24) have shown, the results obtained by water extraction depend largely upon the ratio of soil to water. Therefore, it seemed desirable to use varying ratios of soil to water in the present case. The results are given in tables 8 and 9.

In both soils the displacement method gave higher results for total salts than either the 1:1 or 1:2 water extraction. Evidently the addition of these

TABLE 8

*Total salts and calcium in Miami silt loam obtained by water extraction and displacement*

METHOD USED	AMOUNT IN THE DRY SOIL		
	Total salts before ignition	Total salts after ignition	Calcium
	p. p. m.	p. p. m.	p. p. m.
Displacement.....	261	100	35.6
1:1 extraction.....	211	83	27.1
1:2 extraction.....	234	94	30.4
1:5 extraction.....	311	109	38.6
1:10 extraction.....	377	145	60.8

TABLE 9

*Total salts and calcium in Carrington silt loam as determined by water extraction and displacement*

METHOD USED	AMOUNT IN THE DRY SOIL		
	Total salts before ignition	Total salts after ignition	Calcium
	p. p. m.	p. p. m.	p. p. m.
Displacement.....	551	209	53.9
1:1 extraction.....	450	173	63.4
1:2 extraction.....	470	199	64.2
1:5 extraction.....	582	238	73.1
1:10 extraction.....	646	277	78.5

amounts of water to the soils caused a greater removal of soluble material from solution than was brought into solution by the solvent action of the water. This removal of material from solution is probably caused largely by precipitation due to the change in the nature of the solvent. When larger quantities of water were used the solvent action was greater than the precipitating effect. The point of balance of these factors will probably vary in different soils. It is probable that on some soils a 1:1 water extraction would give higher results than the displacement method. In the two soils studied the 1:5 water extraction gave approximately the same result for total salts as the displacement method.

More calcium was obtained from Miami silt loam by displacement than by a 1:1 or 1:2 water extraction, but this relation does not hold in the case of the Carrington silt loam. This difference is probably due to the calcium being present in different forms in the two soils. The Miami silt loam used was only very slightly acid, while the Carrington silt loam was strongly acid. Some results obtained with phosphorus on these two soils indicate that the phosphorus content of the soil solution is much lower than would be indicated by the usual water extraction.

The results indicate that the displacement method gives the true soil solution. Further studies of this character should give considerable information regarding the value of the water-extraction method for determining the

TABLE 10

*Total salts and nitrate nitrogen in different soils obtained by the water-extraction and displacement methods*

KIND OF SOIL	NO <sub>3</sub> NITROGEN		TOTAL SALTS IN THE DRY SOIL			
	Displacement	Extraction	Before ignition		After ignition	
			Displacement	Extraction	Displacement	Extraction
	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.
Acid peat.....	791.0	840.0	7,484	11,374	2,530	3,965
Neutral peat.....	745.0	690.0	8,940	7,497	3,233	2,618
Clay loam.....	75.2	71.5	747	796	252	281
Superior clay.....	24.7	29.4	301	370	87	121
Plainfield sand.....	22.4	18.7	275	205	75	60
Hancock sand.....	61.2	57.0	1,512	1,400	348	325
Gray silt loam.....	9.7	10.8	161	223	57	124
Miami silt loam.....	71.0	79.8	648	732	222	256
Carrington silt loam.....	54.5	48.3	512	506	173	168
Waukesha silt loam.....	30.4	30.4	340	462	119	186

soluble material in a soil. Before final conclusions can be made regarding the value of the water-extraction method as compared with displacement further investigations will be necessary. These should include determinations of the phosphorus, potassium, calcium and magnesium in a large number of soils by the two methods.

A further comparison of the two methods was made on ten soils by using the 1:5 water extraction on all except the peats. A 1:10 extract was made with the acid peat and a 1:7.5 extract with the neutral peat. The results are shown in table 10 and confirm the conclusions drawn from the preceding data. With some soils the displacement method gave higher results for total salts, while with other soils the water extraction gave the higher results. The results for nitrate nitrogen are the same, within experimental error.

*Discussion of the displacement method*

The results obtained seem to prove that the displacement method gives the true soil solution. It can be used on all soil classes and at a wide range of moisture contents. By using a long soil column small amounts of the soil solution have been obtained from Carrington silt loam at a moisture content of only 6 per cent. The moisture content at which heavy soils can be most conveniently worked is slightly below the optimum for plant growth.

The method has several distinct advantages over other methods which are being used. One of its greatest advantages over the oil pressure method (18) is its simplicity and the fact that it does not require special apparatus. Ordinary glass percolators were entirely satisfactory for most of the work. If it is desirable to reduce the amount of alcohol required the displacement may be started with 200 or 300 cc. of alcohol and after this has penetrated the soil, water may be added to complete the displacement.

The greatest advantage it has over water extracts is that it gives a more correct measure of the material in solution. In addition, the solution obtained is about twenty times as concentrated as the water extract. This greatly reduces the time required for evaporation in all determinations. Five cubic centimeters was generally sufficient for a colorimetric nitrate determination and 25 cc. for a total salt determination.

The two main disadvantages of the method are the time required for displacement and the necessity of using a larger soil sample than is required by the water-extraction method. The time factor is best controlled by experience and care in packing the soil. About five times as much soil must be used as is required for water extraction.

The method seems to deserve much greater attention than it has received in the past. By its use considerable information may be obtained regarding the concentration, composition, and reaction of the true soil solution. It may also afford information that may be of value in studying results which have been obtained by water extraction and other methods.

Results obtained with the displacement method indicate that at ordinary moisture contents the concentration of the soil solution is inversely proportional to the moisture content of the soil. This does not agree with the conclusions which Bouyoucos and McCool made from results obtained with the freezing-point method. A study of the freezing-point method was therefore made to determine the cause of this disagreement.

## THE FREEZING-POINT METHOD

The freezing-point method as a means of determining the concentration of the soil solution directly in the soil was first used by Bouyoucos and McCool (5, 6). It has since been used by Hoagland (13) in studying changes in the salt content of soils due to seasons and cropping. He compared results obtained by this method with those of Stewart (24) who used the water-

extraction method. The two methods gave the same general indications regarding the changes which took place in the salt content of the soils, but the water-extraction method gave from 1.5 to 5 times as much total salts as was indicated by the freezing-point method to be actually in the soil solution.

The freezing-point method as a means of measuring the concentration of the soil solution in the soil is based upon the principle that material in solution causes a depression of the freezing point of the solvent. The assumption was made that the finely divided material of the soil does not affect the freezing-point of the soil solution.

In determinations of the freezing-point depressions of soils at varying moisture contents, Bouyoucos and McCool (6) obtained results which, contrary to what would be expected, indicate that the concentration of the soil solution is not inversely proportional to the moisture content of the soil. The lowering of the freezing point of soils was found to increase approximately in geometric progression as the moisture content decreased in arithmetic progression. This was explained by the following hypothesis:

The hypothesis assumes that a portion of the water found in the soils is inactive and does not take part in dissolving the salts in the soil, and is removed from the field of action as far as the lowering of the freezing point is concerned. Under this assumption the increase of the freezing-point depression is a geometric progression as the percentage of water increases in an arithmetic progression is explained as follows: If a clay soil, for instance, causes 15 per cent of water to become inactive, and this clay at 39 per cent of moisture produces a lowering of the freezing point of  $0.075^{\circ}\text{C}$ . and at 22 per cent  $0.987^{\circ}\text{C}$ ., then at the former moisture content there is 24 per cent of water free or available to dissolve the salts in the soil, while at the latter water content there is only 7 per cent available for the same purpose. It would be natural, therefore, that the depression of the freezing point would be many times greater at the low moisture content than at the high, than would be expected from the difference in the total moisture content, just as the experimental data really indicate.

This hypothesis also assumes (and the assumption seems to have been proved) that the percentage of inactive water is greater at the low than at the high moisture content and tends to decrease from the former to the latter.

Results obtained with the displacement method indicate that all of the water in the soil acts as a solvent and that there must be another explanation of the results obtained with the freezing-point method.

*The concentration of the soil solution at varying moisture contents as determined by the freezing-point and displacement methods*

It has already been shown in tables 4, 5, and 6 that, as determined by the displacement method, the concentration of the soil solution is inversely proportional to the moisture content of the soil. Freezing-point determinations were made at the same time on these soils. Having determined the freezing-point depression of the soil and of the displaced solution, the value for  $K$  can be calculated for both, using the equation  $M.D = K$ . In each case  $M$  is the moisture content of the soil and  $D$  is the freezing-point depression of the



soil or the displaced soil solution. If the concentration of the soil solution is inversely proportional to the moisture content  $K$  should be a constant. If  $K$  is not a constant it indicates that the concentration of the soil solution is not inversely proportional to the moisture content or that there is another factor influencing the freezing-point depression. The value of  $K$  for the displaced solution and the soil should be the same if the freezing-point depression in both cases is caused entirely by the salts in the soil solution. If the values for  $K$  are not the same it indicates that there are other factors affecting the freezing-point depression of the soil. The results obtained with Miami silt loam are given in table 11. Results similar to those given were obtained with Plainfield sand and Carrington silt loam.

The data show that the two methods give an entirely different indication of the concentration of the soil solution, particularly at the lower moisture contents, if it is assumed that the depression is due entirely to material in solution. At a moisture content of 10.30 per cent the freezing-point depression of the soil

TABLE 11

*The freezing-point depression of Miami silt loam and the displaced soil solution at different moisture contents*

MOISTURE CONTENT	FREEZING-POINT DEPRESSION OF SOIL	FREEZING-POINT DEPRESSION OF SOLUTION	$K$ FOR SOIL	$K$ FOR SOLUTION
<i>per cent</i>	<i>°C.</i>	<i>°C.</i>		
10.30	0.460	0.039	4.738	0.401
13.55	0.257	0.030	3.482	0.406
17.25	0.100	0.022	1.725	0.379
20.62	0.057	0.018	1.175	0.371
29.41	0.028	0.013	0.676	0.382
34.05	0.016	0.012	0.544	0.408

indicates a concentration almost twelve times as great as is indicated by the freezing-point depression of the displaced soil solution. At the highest moisture content the two methods give nearly the same result. There are two possible explanations for the results obtained, viz., (a) the inactive or unfree water,<sup>2</sup> which is not supposed to act as a solvent, may be displaced and dilute the other portion of the soil solution; (b) the soil may not cause water to become inactive as a solvent but the finely divided solid material of the soil may cause a depression of the freezing point in addition to that caused by materials in solution.

The first explanation is plausible in that it is possible to displace small amounts of the soil solution at such low moisture contents that there would probably be no free water present. However, with this explanation it would be necessary to assume that unfree water is free to move capillarily. In fact, this assumption is necessary if the displacement method gives a true aliquot

<sup>2</sup> In this paper the terms free and unfree or inactive water are used with the meanings attached to them by Bouyoucos and McCool (6), and by Bouyoucos (3).

of the soil solution. It does not seem probable that a portion of the water would be unable to act as a solvent and at the same time be capable of capillary movement. Therefore, the second explanation may be more nearly correct than the first, as is further indicated in the following.

It is well known that colloidal solutions have the same freezing point as pure water. However, such determinations are not comparable to determinations of the freezing-point depressions of soils in which the amount of liquid present is reduced until it is all in the capillary or film condition. In a review of the literature, the writer did not find any investigations in which a deliberate study was made of the effect of finely divided material on the freezing point when the amount of liquid was so reduced. Foote and Saxton (11, 12) however, in studying the forms of water in certain hydrogels by the dilatometer method, recognized that the hydrogels caused a depression of the freezing point of the capillary water. (They defined capillary water as that water which would not freeze at  $0^{\circ}\text{C}.$ , but could be frozen at lower temperatures.) Van Bemmelen and other investigators (27) have shown that water in hydrogels has a low vapor pressure. Zsigmondy, Bachmann, and Stevenson (26) have shown that the same is true for alcohol and benzene in alcogels and benzogels. If the vapor pressure of a liquid is lowered, its freezing point also is lowered. It therefore seemed probable that the solid material of the soil may cause a depression of the freezing point of the soil solution. The results shown in table 11 indicate that this is the case. In order to obtain more conclusive data on the question, a study was made of the effect of finely divided materials on the freezing point of water, benzene and nitrobenzene. A portion of the results are presented here, but for a more detailed discussion of the procedure and results the reader is referred to another article (20).

In order to study the effect of finely divided materials upon the freezing point of liquids it is desirable to have the solid material as free as possible of substances soluble in the liquids. The materials used fulfilled this requirement very well, as is indicated by the freezing-point depressions at the highest moisture contents.

The  $\text{Fe}(\text{OH})_3$  was prepared by precipitation with  $\text{NH}_4\text{OH}$  from a cold dilute solution of the chloride. It was washed free of chlorides, air-dried and ground to pass a 200-mesh screen. The percentage of water in the  $\text{Fe}(\text{OH})_3$  is expressed on the air-dry basis. In all other cases the percentage of liquid is expressed on the oven-dry basis.

Baker's C. P.  $\text{Al}_2\text{O}_3$  was used. It contained some material soluble in water but nothing soluble in benzene or nitrobenzene.

#### *The freezing-point depression of water in finely divided material*

The freezing-point depression of water in  $\text{Fe}(\text{OH})_3$  and Carrington silt loam was determined at varying moisture contents. The results are shown in table 12.

The results indicate a considerable depression due to the solid material. The effect due to soluble material was probably small, especially in the case of the  $\text{Fe}(\text{OH})_3$ , since this material gave a depression of only  $0.004^\circ\text{C}$ . at a moisture content of 100 per cent. In order to explain the results obtained with  $\text{Fe}(\text{OH})_3$  by the hypothesis that it rendered part of the water unfree, it would be necessary to assume that at a moisture content of 15 per cent 14.85 per cent of water was unfree and only 0.15 per cent of water was acting as a solvent as is indicated by the following calculations. Solving for  $K$  in the equation  $M \cdot D = K$  when  $M$  is 100 and  $D$  is  $0.004^\circ\text{C}$ ., the value of  $K$  is 0.400. Taking this value for  $K$  and solving for  $M$  when the freezing-point depression is  $2.668^\circ\text{C}$ . one obtains 0.15 as the value of  $M$ . In this case  $M$  is the percentage of water which would be acting as a solvent at the moisture content at which a depression of  $2.668^\circ\text{C}$ . is secured. The inactive water would be obtained by difference and found to be 14.85 per cent. A similar

TABLE 12

*The freezing-point depression of water in  $\text{Fe}(\text{OH})_3$  and in Carrington silt loam at varying moisture contents*

$\text{Fe}(\text{OH})_3$		CARRINGTON SILT LOAM	
Moisture content	Freezing-point depression	Moisture content	Freezing-point depression
<i>per cent</i>	<i>°C.</i>	<i>per cent</i>	<i>°C.</i>
15.0	2.668	9.0	1.622
17.5	1.651	11.5	0.585
20.0	0.393	14.0	0.315
22.5	0.177	16.5	0.213
25.0	0.086	21.5	0.113
37.5	0.016	26.5	0.062
50.0	0.009	31.5	0.030
100.0	0.004	46.5	0.021

calculation for the soil shows that at a moisture content of 9.0 per cent it would be necessary to assume that only 0.60 per cent water was free and that 8.40 per cent was unfree.

*The freezing-point depression of benzene and nitro-benzene in  $\text{Al}_2\text{O}_3$  and Carrington silt loam*

The use of organic liquids in which most inorganic salts are insoluble makes it possible to eliminate entirely the depression due to soluble materials. Benzene and nitrobenzene were chosen because they are readily obtained and freeze at a convenient working temperature. The results obtained with these liquids in Carrington silt loam and aluminium oxide are given in tables 13 and 14.

The results are of the same order as was obtained with the same solid material and water. Since there is no material in solution it seems that the

only possible explanation of the results is that the solid material causes a depression of the freezing point of the liquids when they are in the film or capillary condition, but does not affect their freezing point at contents above saturation. If this is the correct explanation for the results obtained with these liquids it is undoubtedly the explanation for the results obtained with soils. It may therefore be concluded that at ordinary moisture contents the freezing-point depression of the soil solution in the soil is caused by two factors, the material in solution, and the finely divided solid material of the soil.

TABLE 13

*The freezing-point depression of benzene in Carrington silt loam and aluminium oxide*

CARRINGTON SILT LOAM		ALUMINIUM OXIDE	
Benzene	Freezing-point depression	Benzene	Freezing-point depression
<i>per cent</i>	$^{\circ}\text{C.}$	<i>per cent</i>	$^{\circ}\text{C.}$
5.0	0.660	30.0	1.337
7.5	0.355	35.0	0.682
10.0	0.150	40.0	0.492
12.5	0.060	45.0	0.326
15.0	0.033	50.0	0.212
20.0	0.025	55.0	0.115
25.0	0.010	65.0	0.052
37.5	0.000	75.0	0.030
		100.0	0.000

TABLE 14

*The freezing-point depression of nitrobenzene in Carrington silt loam and aluminium oxide*

CARRINGTON SILT LOAM		ALUMINIUM OXIDE	
Nitrobenzene	Freezing-point depression	Nitrobenzene	Freezing-point depression
<i>per cent</i>	$^{\circ}\text{C.}$	<i>per cent</i>	$^{\circ}\text{C.}$
12.5	1.630	50.0	1.720
15.0	1.200	60.0	1.175
17.5	0.780	70.0	0.810
20.0	0.510	80.0	0.580
25.0	0.230	90.0	0.340
30.0	0.130	100.0	0.200
37.5	0.075	150.0	0.020
50.0	0.000	200.0	0.000

*The relation between the freezing-point depression due to solid material and that due to material in solution*

In order to determine whether or not the depression due to solid material and that due to material in solution are additive in their effect on the freezing point, samples of aluminium oxide were moistened with water and other samples were moistened with a sugar solution which had a freezing-point

depression of  $0.126^{\circ}\text{C}$ . A sugar solution was used because there is no possibility of a chemical reaction between the sugar and aluminium oxide. If the two factors are additive the difference between the freezing-point depressions at any moisture content should be  $0.126^{\circ}\text{C}$ ., the depression due to sugar. Adsorption may influence the results to some extent. The differences obtained are given in the last column of table 15.

These results and others obtained when sugar solutions and a  $\text{Ca}(\text{NO}_3)_2$  solution were used in soils, kaolin, silica and ferric hydroxide, prove that the two factors are very nearly additive in their effect on the freezing point. The differences found at the three lower moisture contents are easily within the limit of experimental error, which is quite large at low moisture contents. The presence of sugar did not affect the general order of results.

The results afford further evidence that the great increase in the freezing-point depression at the lower moisture contents is not due to part of the water being withdrawn from the rôle of a solvent by the solid material. If the

TABLE 15

*The freezing-point depression of water and a sugar solution in aluminium oxide at different moisture contents*

MOISTURE CONTENT	FREEZING-POINT DEPRESSION WITH WATER	FREEZING-POINT DEPRESSION WITH SOLUTION	FREEZING-POINT DEPRESSION DUE TO THE SUGAR
<i>per cent</i>	$^{\circ}\text{C}$ .	$^{\circ}\text{C}$ .	$^{\circ}\text{C}$ .
25.0	2.118	2.290	0.172
30.0	1.227	1.312	0.075
35.0	0.650	0.740	0.090
40.0	0.370	0.500	0.130
50.0	0.220	0.344	0.124
75.0	0.075	0.195	0.120
100.0	0.053	0.173	0.120

aluminium oxide had rendered any of the water unfree the solution would have been greatly concentrated at the lower moisture contents and the depression due to the sugar would have been many times that shown in the table. The depression of the freezing point of water at 25 per cent was forty times as great as at 100 per cent. If this had been caused by part of the water being withdrawn from the rôle of a solvent, and the same amount had been withdrawn when the sugar solution was added, the depression of the sugar solution at 25 per cent would have been  $6.920^{\circ}\text{C}$ . instead of  $2.290^{\circ}\text{C}$ . The depression due to the sugar alone at this moisture content would have been  $4.802^{\circ}\text{C}$ . instead of only  $0.172^{\circ}\text{C}$ ., the experimental value.

*The freezing-point depression of soils at their moisture equivalent*

The freezing-point depression of soils at medium to low moisture contents is caused in large part by the solid material. The force which holds the water on the soil particles probably causes the freezing-point depression. If a num-

ber of soils are subjected to the same centrifugal force, and come to an equilibrium with this force, they will retain different percentages of water. These different percentages of water which are retained will be held with equal forces in the different soils. Since this same force probably causes the freezing-point depression, it should be possible to reduce all soils to the same freezing-point depression, after the removal of soluble salts, by subjecting them to the same centrifugal force.

In a determination of the moisture equivalent of soils the soil is subjected to a centrifugal force of 1000 times gravity. The moisture content after centrifuging is that at which the force of attraction between the soil and water is equal to this centrifugal force. In this manner the force holding water in different soils may be brought to a uniform value. Therefore the freezing-point depression of the soils, due to solid material, should be equal at the moisture contents represented by their moisture equivalents.

TABLE 16  
*The freezing-point depression of washed soils at their moisture equivalent*

SOIL	MOISTURE EQUIVALENT	FREEZING-POINT DEPRESSION °C.
Carrington silt loam.....	21.57	0.055
Knox silt loam.....	25.40	0.057
Mellen loam.....	16.39	0.053
Superior clay.....	21.84	0.061
Plainfield sand.....	4.73	0.076
Miami silt loam.....	26.47	0.052
Silty clay loam.....	33.29	0.061
Fine sandy loam.....	12.49	0.057
Peat.....	111.60	0.061
Kaolin.....	38.12	0.046
Silica.....	19.14	0.057
Aluminium oxide.....	21.56	0.043

In order to determine the freezing-point depression due to solid material it is necessary to remove the soluble material as far as possible. One-hundred-gram samples of different soils, silica, kaolin and aluminium oxide were washed with 1200 to 1500 cc. of distilled water to remove soluble salts. The samples were then dried in an electric oven at 105°C. The moisture equivalent was determined in the usual manner. After centrifuging the freezing-point determinations were made on the soils. The speed of the centrifuge was slightly less than that which gives a force of 1000 times gravity. This caused slightly high results for the moisture equivalent and hence low results for the freezing-point depression, due to solid material, at the true moisture equivalent. There were undoubtedly several sources of error, such as the incomplete removal of the soluble material, puddling in making the determination of the moisture equivalent, and evaporation in transferring the soil from the moisture cups to the freezing-point tubes. The results are shown in table 16.



The results indicate that at the moisture equivalent the depression of the freezing point due to solid material is very nearly the same in different soils and certain artificial materials. This can be explained only by the assumption that the same force which retains the moisture causes the freezing-point depression. The values are not exactly the same but are within experimental error. The low values for kaolin and aluminium oxide are probably due to the fact that these materials pack very tightly in the centrifuge preventing the water from being readily thrown out. The high result for the Plainfield sand may be due to the extreme readiness with which the water is removed from such a coarse soil.

The results indicate that the freezing-point method could be used to determine the salt content of soils at their moisture equivalent. At the moisture equivalent the depression due to solid material is probably a constant, about  $0.050^{\circ}\text{C}$ . By determining the freezing-point depression of a soil at its moisture equivalent and subtracting this constant, the freezing-point depression due to soluble material would be obtained. In using such a procedure great care should be taken that the true moisture equivalent is used in all cases, for a slight error in the moisture content would decidedly affect the freezing-point depression due to solid material. This procedure is rather long, so it is doubtful if it would be of much value. If the freezing-point method is used it would be more convenient and probably more accurate to make the determinations at moisture contents above saturation, entirely eliminating the depression caused by the solid material.

#### *Discussion of the freezing-point method*

The freezing-point method does not give a measure of the concentration of the soil solution in the soil at ordinary moisture contents, for it has been shown that finely divided material causes a depression of the freezing point of a liquid in the film or capillary condition. The force holding the liquid on the solid material and causing the freezing-point depression is adhesion. When the amount of water in the soil is increased a point is reached at which some of the soil solution is so distant that this force no longer affects its freezing point. This point is probably the point of saturation. Probably at any moisture content below saturation the solid material causes a depression of the freezing point of the soil solution. At moisture contents above saturation the depression becomes due entirely to material in solution.

The freezing-point method has been used by Bouyoucos and his associates to determine the lime requirement of soils (1), the velocity of reactions between soils and chemical reagents (4), the solubility of soils (2), and the absolute salt content of soils (7). In these investigations the moisture content was always very high, varying from 66 to several hundred per cent. At those moisture contents the depression is due entirely to materials in solution and the method gives a satisfactory measure of the soluble material present. It is well adapted to such studies and used under these conditions has given valuable results.

## SUMMARY

It is desirable in studying problems of soil fertility, plant nutrition and related subjects to have a method with which the true soil solution may be obtained from a soil at ordinary moisture contents in sufficient quantities for analytical work. In a review of the literature it was found that Ischerekov (15), using the displacement method, obtained results which indicate that the method gives the true soil solution in quantities sufficient for most purposes. Hence it seemed desirable to make a study of the method and compare it with other methods which are now being used in studying the concentration and composition of the soil solution.

The method consists of packing the moist soil in a cylinder provided with an outlet at the bottom. Ethyl alcohol is then poured on top of the soil column and as it penetrates the soil it displaces some of the soil solution which forms a zone of saturation below the alcohol. This zone increases in depth as it is continually forced downward by the alcohol. When the saturated zone reaches the bottom of the soil column the clear soil solution, free of alcohol, drops from the soil as gravitational water.

A study was made of the effect of different displacing liquids on the time required for displacement, the percentage of the soil solution displaced and the composition of the displaced solution. The concentration of successive portions of the displaced soil solution was determined and also the concentration of the soil solution obtained from the soils at different moisture contents. The amount of total salts, nitrates, and calcium obtained from the soil by displacement was compared with the amount secured from the soil by water extraction.

Results obtained with the displacement method did not agree with the conclusions of Bouyoucos and McCool (6), drawn from a study of the freezing-point depressions of soils, with regard to the concentration of the soil solution at different moisture contents and the forms of water in the soil. Therefore a study was made of the freezing-point method and factors affecting the freezing-point depression of the soil solution in the soil. The effect of finely divided material on the freezing point of water, benzene and nitrobenzene was studied. A summary of the results and conclusions is given below.

(a) Ethyl alcohol was found to be more satisfactory as a displacing liquid than water, methyl alcohol, acetone, or liquids non-miscible with water.

(b) The composition of the soil solution obtained by displacement was not influenced by the displacing liquid used.

(c) Successive portions of the displaced solution gave the same freezing-point depression and contained the same amount of total salts.

(d) The concentration of the displaced solution was found to be inversely proportional to the moisture content of the soil.

(e) The displacement method gave the same amount of nitrate nitrogen and approximately the same amount of total salts as a 1:5 water extraction of the soil.

(f) The method seems to be well adapted to a study of the composition and reaction of the soil solution under any condition.

(g) Finely divided material was found to cause a depression of the freezing point of water, benzene, and nitrobenzene when the amount of liquid was reduced until it was in the film or capillary condition.

(h) The freezing-point method does not give a measure of the concentration of the soil solution directly in the soil at ordinary moisture contents of the soil.

(i) At high moisture contents, probably only above saturation, the freezing-point method gives a measure of the concentration of the soil solution.

(j) The freezing-point depression due to solid material at the moisture equivalent was found to be very nearly a constant for a number of soils.

(k) A soil does not cause a considerable amount of water to be removed from the role of a solvent, as has sometimes been assumed.

A subsequent article will be devoted to the classification of the soil moisture

#### REFERENCES

- (1) BOUYOUCOS, G. J. 1916 The freezing point method as a new means of determining the nature of soil acidity and the lime requirement of soils. Mich. Agr. Exp. Sta. Tech. Bul. 27.
- (2) BOUYOUCOS, G. J. 1919 Rate and extent of solubility of soils under different treatments and conditions. Mich. Agr. Exp. Sta. Tech. Bul. 44.
- (3) BOUYOUCOS, G. J. 1921 A new classification of the soil moisture. *In* Soil Sci., v. 11, no. 1, p. 33-49.
- (4) BOUYOUCOS, G. J., AND LAUDEMAN, W. A. 1917 The freezing point method as a new means of studying the velocity of reaction between soils and chemical reagents and the behavior of equilibrium. Mich. Agr. Exp. Sta. Tech. Bul. 37.
- (5) BOUYOUCOS, G. J., AND MCCOOL, M. M. 1915 The freezing point method as a new means of measuring the concentration of the soil solution directly in the soil. Mich. Agr. Exp. Sta. Tech. Bul. 24.
- (6) BOUYOUCOS, G. J., AND MCCOOL, M. M. 1916 Further studies on the freezing-point lowering of soils. Mich. Agr. Exp. Sta. Tech. Bul. 31.
- (7) BOUYOUCOS, G. J., AND MCCOOL, M. M. 1918 Determining the absolute salt content of soils by the freezing point method. *In* Jour. Agr. Res., v. 15, p. 331-336.
- (8) BRIGGS, L. J., AND MCCALL, A. G. 1904 An artificial root for inducing capillary movement of soil moisture. *In* Science, v. 20, p. 566-569.
- (9) CAVERS, F. G. 1914 Gola's theory of Edaphism. *In* Jour. Ecol., v. 2, p. 217.
- (10) DAVIS, R. O. E., AND BRYAN, H. 1910 An electrical bridge for the determination of soluble salts in soils. U. S. Dept. Agr. Bur. Soils Bul. 61.
- (11) FOOTE, H. W., AND SAXTON, B. 1916 The effect of freezing on certain inorganic hydrogels. I. *In* Jour. Amer. Chem. Soc., v. 38, no. 3, p. 588-609.
- (12) FOOTE, H. W., AND SAXTON, B. 1917 The effect of freezing on certain inorganic hydrogels: II. *In* Jour. Amer. Chem. Soc., v. 39, no. 6, p. 1103-1125.
- (13) HOAGLAND, D. R. 1918 The freezing-point method as an index of variations in the soil solution due to season and crop growth. *In* Jour. Agr. Res., v. 12, no. 6, p. 369-395.
- (14) HOAGLAND, D. R., MARTIN, J. C., AND STEWART, G. R. 1920 Relation of the soil solution to the soil extract. *In* Jour. Agr. Res., v. 20, no. 5, p. 381-395.

- (15) ISCHEREKOV, V. 1907 Obtaining the soil solution in an unaltered condition. *In* Zhur. Oputn. Agron. (Russ. Jour. Exp. Landw.), v. 8, p. 147-166.
- (16) LIPMAN, C. B. 1918 A new method of extracting the soil solution. Univ. Cal. Pub. Agr. Sci., v. 3, no. 7, p. 131-134.
- (17) MITSCHERLICH, E. A. 1907 Eine chemische Bodenanalyse für pflanzenphysiologische Forschungen. *In* Landw. Jahrb., Bd. 36, p. 309-369.
- (18) MORGAN, J. F. 1916 The soil solution obtained by the oil pressure method. Mich. Agr. Exp. Sta. Tech. Bul. 28.
- (19) NORTHRUP, Z. 1918 The true soil solution. *In* Science, v. 47, p. 638-639.
- (20) PARKER, F. W. 1921 The effect of finely divided material on the freezing point of water, benzene, and nitrobenzene. *In* Jour. Amer. Chem. Soc., v. 43, No. 5, p. 1011-1018.
- (21) RAMANN, E., MÄRZ, S., AND BAUER, H. 1916 The soil solution obtained by the action of a hydraulic press. *In* Internat. Mit. Bodenk., Bd. 6, p. 27; *abs. in* Chem. Abs., v. 11, p. 3078. (Original not seen.)
- (22) SCHLOESING, TH. 1866 Sur l'analyse des principes solubles de la terre végétale. *In* Compt. Rend. Acad. Sci. (Paris), t. 63, p. 1007.
- (23) SCHREINER, O., AND FAIRYER, G. H. 1905 Colorimetric, turbidity, and titration methods used in soil investigations. U. S. Dept. Agr. Bur. Soils Bul. 31, p. 16-17.
- (24) STEWART, G. R. 1918 Effect of season and crop growth on modifying the soil extract. *In* Jour. Agr. Res., v. 12, no. 6, p. 311-369.
- (25) VAN SUCHTELEN, F. H. H. 1912 Methode zur Gewinnung der natürlichen bodenlösung. *In* Jour. Landw., Bd. 60, p. 669-70.
- (26) ZSIGMONDY, R., BACHMANN, W., AND STEVENSON, E. J. 1912 Ueber einen Apparat zur Bestimmung der Dampfspannungsisothermen des Gels der Kieselsäure. *In* Ztschr. Anorg. Chem., Bd. 75, p. 189-197.
- (27) ZSIGMONDY, D., AND SPEAR, E. B. 1917 The Chemistry of Colloids., chap. 7. Wiley, New York.

## THE EFFECT OF STRAW ON THE BIOLOGICAL SOIL PROCESSES<sup>1</sup>

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### INTRODUCTION

In the wheat country of Eastern Washington, the addition of straw is practically the only method, under the present practices of farming, of returning humus to the soil. It is a common observation that the addition of wheat straw to the soil decreases the following crop yield. The practice of burning wheat stubble on the farm is common, but such procedure is detrimental to permanent agriculture. It is therefore important to determine why the addition of straw to the soil does cause a decrease in the following crop yield and whether any practice will overcome the loss. It was with this purpose in view that the work was taken up.

### HISTORICAL

The following discussion refers to the work that has been done on the effect of straw and allied materials upon soils under various conditions.

Störmer (10) showed that in a series of pot experiments on heavy and light soils, the addition of straw to green manure reduced the efficiency of the nitrogen in the green manure. The second year the results were better. Straw alone reduced the yield—the finer the straw the smaller the yield. The addition of carbon bisulfide to the soil to which straw had been added doubled the yield.

Von Seelhorst and Freckmann (13) worked on the effect of aeration and moisture upon the addition of straw and strawy manures on loam and sandy soils in pots. Their work showed that when nitrates were applied denitrification was proportional to the applications of straw. In the case of the loam, the application of straw alone was more injurious.

Von Seelhorst and Freckmann (14) showed that the addition of lime and sulfuric acid lessens the injurious effect of straw on the yield, but does not overcome it.

Stutzer (11) carried on pot experiments with buckwheat followed by mustard to determine whether the injurious effects caused by the addition

<sup>1</sup> Contribution from the Washington Agricultural Experiment Station, State College of Washington, Pullman, Washington.

of straw and similar organic substances could be overcome by the addition of ammonium sulfate. He found the growth poorer with ammonium sulfate than with sodium nitrate. The addition of calcium carbonate increased the injurious effect of the ammonium sulfate.

Chirikov and Shmuk (3) experimented on the influence of moisture and straw upon denitrification in sandy loam. The work was carried out in pots. At a constant moisture the yield of oats decreased as the straw was increased, and as the moisture decreased the yield decreased. The addition of calcium carbonate with the straw decreased the injurious effect of the straw but did not overcome it. The authors hold that the diminished yield is not due to denitrification in the strict sense, but that nitrates are converted into insoluble nitrogen compounds which are less assimilable by the plants.

Bischoff (1) conducted pot experiments at Göttingen, in which he turned under straw, 10 weeks, 4 weeks, and immediately before planting. He grew mustard and buckwheat on a sandy and a clayey soil. He found that on the sandy soil the use of straw was practically always followed by a smaller yield of dry matter and of nitrogen. The injurious effect was less in the presence of sodium nitrate. On clayey soils the straw did not uniformly decrease the yield. With sodium nitrate the early application of straw produced the greatest depression in yield. In the absence of sodium nitrate the late application of straw caused the greatest loss.

Löhnis and Green (7) state that "straw humus interfered with the process of nitrification in the same manner as the undecomposed straw."

Von May (12), worked on the effect of straw fertilizers on potatoes. He states "the results show that the availability of organically combined nitrogen was depressed by the presence of a nitrogen-free organic substance," as in the case of straw. He suggests that the loss in available nitrogen is due to the appropriation of the soluble nitrogen by microorganisms which use the nitrogen-free substances as sources of energy.

Doryland (4) reports, as a result of his tests:

Oats grown in pots containing quartz sand are greatly reduced in yield when dextrose is added in the presence of limited amounts of plant food. When dextrose is added in the presence of abundant plant food the reduction in oat yield is less. Soils have a definite ammonia and nitrate consuming power. The addition of dextrose or straw temporarily increases it. When large quantities of straw (20 tons to the acre) are added to soil, there is a marked decrease in the ammonifying power and a marked increase in the ammonia and nitrate-consuming power. Plowing under crop residues affects the soil in a similar way, but to a less extent. The disturbing influence of organic residue is largely due to the excess energy material with a marked temporary increase in multiplication of microorganisms, and a proportional assimilation of plant food elements followed upon exhaustion of excess energy material, by an increased liberation of plant food. The terms "beneficial" and "detrimental" bacteria when applied to saprophytic organisms have only a relative value. Under a certain proportion of energy to nutrients, the "beneficial" organism may become "detrimental," and vice versa.



## DISCUSSION

There are several possible explanations of what takes place in the soil after the addition of wheat straw. The addition of cellulose to the soil in the form of wheat straw may have a toxic effect on the nitrate-forming bacteria and thus inhibit the formation of nitrates. It may be that the cellulose-fermenting organisms use up the nitrates as a food for themselves and thus lower the nitrogen supply of the plants. Another point that suggests itself is that the straw acts as a source of energy to a host of soil bacteria, which then use the nitrates as their source of nitrogen, build up organic nitrogen, probably throw off nitrogen in the form of organic nitrogenous matter as a waste product, thus deprive the plants of their soluble nitrogenous food.

## OUTLINE OF WORK

The direct object of the work in hand was to find the effect of adding straw to the soil on the biological agents of the soil, to study the effect of straw on different groups of bacteria and their activities, and as a result of these investigations to devise, if possible, some method of adding humus to the soil in the form of wheat straw, without subsequent ill effects. Specifically, the following work was undertaken to study: first, the effect of adding varying amounts of straw to the soil upon nitrate production and upon the total nitrogen content of the soil, to find out whether nitrogen is really lost or merely transformed in the soil; second, the effect of straw upon the number and the type of bacteria in the soil; third, the effect of straw upon nitrogen fixation, ammonification and denitrification; fourth, the isolation of nitrate-forming bacteria and the effect of straw and pure cellulose upon them.

## EXPERIMENTAL

*The effect of different amounts of straw on nitrate formation and the total nitrogen content of the soil<sup>2</sup>*

To 100 gm. of sieved soil<sup>3</sup> contained in glass tumblers, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0 and 5.0 per cent of finely chopped wheat straw was added. The moisture content was adjusted to 19 per cent, and 0.2 gm. of ammonium sulfate was added to each tumbler as well as to a check which received no straw. The work was carried out in duplicate. The tumblers were covered and weighed and incubated at room temperature, about 21°C. The moisture content was adjusted weekly. Determinations of the nitrate content by the zinc-iron reduction method (6), and the total nitrogen by the modified Gunning method to include nitrates, were made immediately, and at the end of 6, 12, 18 and 24 weeks.

<sup>2</sup> Credit is due Mr. Milton Brandt for most of the analyses in this section.

<sup>3</sup> All soil used was Palouse field soil.

From an analysis of tables 1, 2 and 3, it is apparent that the addition of wheat straw has an effect on the formation of nitrates in the soil under laboratory conditions. After the 6 and 12-week periods, straw between the

TABLE 1  
*Nitrate nitrogen per 100 gm. of soil—Average of two determinations*

AMOUNT OF STRAW ADDED	AT BEGINNING	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS	END OF 24 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	9.72	12.25	22.84	27.58	23.52
0.2	9.72	14.81	22.82	32.76	25.56
0.3	9.72	15.12	21.84	34.10	23.38
0.4	9.72	14.91	19.88	27.16	25.38
0.5	9.72	13.86	21.28	31.78	25.76
0.6	9.72	16.36	21.70	31.78	23.10
0.7	9.72	13.16	22.68	29.26	21.60
0.8	9.72	12.04	19.60	27.02	22.12
0.9	9.72	12.18	20.66	27.86	22.02
1.0	9.72	13.72	15.54	32.28	22.54
2.0	9.72	11.06	13.58	27.02	18.48
3.0	9.72	12.42	14.00	19.28	16.52
4.0	9.72	9.26	8.68	18.62	14.56
5.0	9.72	7.84	9.52	13.36	7.56
Check	9.72	13.44	19.74	34.72	26.74

TABLE 2  
*Increase or decrease in nitrate nitrogen over the nitrate nitrogen in the beginning*

AMOUNT OF STRAW ADDED	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS	END OF 24 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	2.53	13.12	17.86	13.80
0.2	5.09	13.10	23.04	15.84
0.3	5.40	12.12	24.38	13.66
0.4	5.19	10.16	17.44	15.66
0.5	4.14	11.56	22.06	16.04
0.6	6.64	11.98	22.06	13.38
0.7	3.44	13.92	19.54	11.88
0.8	2.32	9.88	17.30	12.40
0.9	2.46	12.44	16.14	12.30
1.0	4.00	5.82	22.56	12.82
2.0	1.32	3.86	17.30	8.76
3.0	2.70	4.28	9.56	6.80
4.0	-0.46	0.96	8.90	4.84
5.0	-1.88	-0.20	3.64	-1.16
Check	3.72	10.02	25.00	17.02

amounts of 0.1 per cent and 0.7 per cent actually stimulated the formation of nitrates over that in the check to which no straw had been added. After the 18 and 24-week periods, in every case there was a loss in nitrate formation over the check.

Table 4 shows that if straw inhibits the formation of nitrates or actually causes a decrease in the original nitrate content, as is the case with the 4 and 5 per cent straw, there is no loss in total nitrogen in the soil. The nitrates

TABLE 3  
*Increase or decrease in nitrate nitrogen over the increase in the check for each period*

AMOUNT OF STRAW ADDED	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS	END OF 24 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	-1.29	3.10	-7.14	-3.22
0.2	1.37	3.08	-1.96	-1.18
0.3	1.68	2.10	-0.62	-3.36
0.4	1.47	0.14	-7.56	-1.36
0.5	0.42	0.54	-2.94	-0.98
0.6	1.70	0.96	-2.94	-3.64
0.7	0.72	2.94	-5.46	-5.14
0.8	-1.40	-0.14	-7.70	-4.62
0.9	-1.36	0.42	-6.86	-4.72
1.0	0.28	-4.30	-2.44	-4.20
2.0	-2.38	-6.39	-7.70	-8.26
3.0	-1.02	-5.94	-15.44	-10.22
4.0	-4.28	-9.06	-16.10	-12.18
5.0	-5.86	-10.22	-21.36	-19.18

TABLE 4  
*Total nitrogen per 10 gm. of soil—Average of two determinations*

AMOUNT OF STRAW ADDED	AT THE BEGINNING	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS	END OF 24 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	17.35	19.25	23.03	26.95	20.83
0.2	17.71	19.67	23.98	28.28	24.01
0.3	17.29	20.58	23.13	25.20	20.02
0.4	17.71	19.76	21.77	30.66	19.57
0.5	19.18	20.93	28.42	28.07	20.08
0.6	17.78	19.81	26.45	27.02	19.39
0.7	18.06	18.48	23.80	25.55	19.71
0.8	18.34	18.69	26.04	23.03	19.11
0.9	19.32	20.02	23.66	23.80	20.02
1.0	19.28	18.96	23.80	25.99	21.19
2.0	18.34	20.51	23.45	26.04	20.55
3.0	18.06	22.33	24.12	27.09	21.16
4.0	18.11	21.49	25.13	24.22	21.16
5.0	18.90	20.65	21.63	25.84	20.81
Check	18.20	19.53	21.98	25.55	19.97

are probably transformed to organic nitrogenous matter, and there is no loss in total nitrogen due to the straw. The amounts of nitrogen vary somewhat but the amounts at the end of each period do not lie very far apart. The addition of straw in no way interferes with the normal increase in total nitrogen.

In order to check up on this work and to find out what happens after the 24-week period, the work was repeated covering a 48-week period. The analyses were made for nitrates and total nitrogen every 6 weeks.

TABLE 5  
*Nitrate nitrogen per 100 gm. of soil—Average of two determinations*

AMOUNT OF STRAW ADDED	AT BEGINNING	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS	END OF 24 WEEKS	END OF 30 WEEKS	END OF 36 WEEKS	END OF 40 WEEKS	END OF 48 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	10.25	12.16	17.50	19.18	19.32	30.46	25.48	26.04	26.90
0.2	10.25	11.26	17.28	19.32	23.96	27.02	21.98	25.20	27.44
0.3	10.25	10.69	17.50	17.44	25.94	21.56	24.12	25.32	24.92
0.4	10.25	12.13	17.22	17.55	19.78	21.66	23.60	23.52	24.22
0.5	10.25	13.16	18.62	15.92	21.00	24.22	27.30	26.60	24.92
0.6	10.25	11.62	21.84	22.68	26.80	23.47	22.54	23.80	23.80
0.7	10.25	12.60	16.19	12.32	22.60	22.96	22.02	21.00	25.06
0.8	10.25	10.27	13.44	14.65	16.80	17.78	20.02	23.66	18.48
0.9	10.25	10.50	13.58	12.88	17.64	24.92	21.28	23.80	21.56
1.0	10.25	9.80	15.12	24.64	18.76	19.32	18.48	19.04	17.92
2.0	10.25	9.05	12.55	18.90	17.50	13.86	21.72	19.18	17.08
3.0	10.25	9.24	17.36	19.04	14.30	14.98	17.78	17.78	17.08
4.0	10.25	9.52	13.72	17.36	6.86	11.06	9.38	9.38	9.97
5.0	10.25	10.22	13.30	18.64	7.84	7.84	9.80	10.50	10.50
Check	10.25	11.20	14.70	14.28	17.74	17.50	24.36	24.36	24.50

TABLE 6  
*Increase or decrease in nitrate nitrogen over the nitrate nitrogen at the beginning*

AMOUNT OF STRAW ADDED	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS	END OF 24 WEEKS	END OF 30 WEEKS	END OF 36 WEEKS	END OF 40 WEEKS	END OF 48 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	1.91	7.25	8.93	9.07	20.21	15.23	15.79	16.65
0.2	1.01	7.03	9.07	13.71	16.77	11.73	14.95	17.19
0.3	0.24	7.25	9.17	15.69	11.31	13.87	15.07	14.67
0.4	1.88	6.72	7.30	9.52	11.41	13.35	13.27	13.97
0.5	2.91	8.37	5.67	10.74	13.97	17.05	16.35	14.67
0.6	1.37	11.59	12.43	16.55	13.22	12.29	13.55	13.55
0.7	2.35	5.94	2.07	12.35	12.71	11.77	10.75	14.81
0.8	0.02	3.19	4.40	6.55	7.53	9.77	13.41	8.23
0.9	0.25	3.33	2.63	7.39	14.67	11.03	13.55	11.21
1.0	-0.45	4.87	4.39	8.51	9.07	8.23	8.79	7.67
2.0	-1.20	2.30	8.65	7.25	3.61	11.47	9.93	7.73
3.0	-1.01	7.11	8.79	4.05	4.73	7.53	7.53	7.73
4.0	-0.73	3.47	7.11	-3.39	0.81	-1.87	-0.87	-0.28
5.0	-0.03	3.05	8.39	-2.41	-2.41	-0.45	0.25	0.25
Check	0.95	4.45	4.03	7.51	7.49	14.11	14.11	14.25

The data shown in tables 5, 6 and 7 are not as striking as the results obtained previously over the 24-week period. After the 30-week period, however, the results ran very much the same as in the 18 and 24-week periods of the

former set. The loss in nitrate formation after the 30-week period seems to increase with the increase in the straw. This is especially noticeable in the cases where 4 and 5 per cent straw applications were made. It is again evident that the straw has a marked influence on nitrate formation.

TABLE 7

*Increase or decrease in nitrate nitrogen over the increase in the check for each period*

AMOUNT OF STRAW	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS	END OF 24 WEEKS	END OF 30 WEEKS	END OF 36 WEEKS	END OF 40 WEEKS	END OF 48 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	0.96	2.80	4.90	1.46	12.72	1.12	1.68	2.40
0.2	0.06	2.58	5.04	6.20	9.28	-2.38	0.84	2.94
0.3	-0.71	2.80	5.14	8.18	3.82	-0.24	0.96	0.42
0.4	0.93	2.27	3.27	2.01	3.92	-0.76	-0.84	-0.28
0.5	1.96	3.92	1.64	3.23	6.48	2.84	2.24	0.42
0.6	0.42	7.04	8.40	9.04	5.73	-1.82	-0.56	-0.70
0.7	1.40	1.49	-1.96	4.84	5.22	-2.34	-3.36	0.56
0.8	-0.93	-0.26	0.37	-0.96	0.04	-4.34	-0.70	-6.02
0.9	-0.70	-1.12	-1.40	-0.12	7.18	-2.08	-0.56	-3.04
1.0	-0.50	0.42	0.36	1.00	1.58	-5.88	-5.32	-6.58
2.0	-2.15	-2.15	4.63	-0.26	-3.88	-2.64	-4.18	-6.52
3.0	-1.96	2.76	4.76	-3.46	-2.76	-6.58	-6.58	-6.52
4.0	-1.68	0.02	3.08	-10.90	-6.68	-15.98	-14.98	-14.53
5.0	-0.98	-1.40	4.36	-9.92	-9.90	-14.66	-13.86	-14.00
Check								

TABLE 8

*Total nitrogen per 10 gm. of soil—Average of two determinations\**

AMOUNT OF STRAW	AT BEGINNING	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS	END OF 24 WEEKS	END OF 30 WEEKS	END OF 36 WEEKS	END OF 48 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	19.72	21.62	21.91	22.33	23.17	20.44	23.24	18.48
0.2	18.55	21.42	22.19	22.47	24.13	20.48	20.86	19.39
0.3	18.51	19.74	21.56	22.54	24.28	20.33	21.14	20.02
0.4	18.49	21.70	21.77	23.45	24.20	20.79	22.96	20.93
0.5	18.13	19.39	20.23	23.45	24.50	21.00	22.26	22.26
0.6	18.20	20.51	20.44	23.17	22.89	20.44	22.82	22.64
0.7	18.13	21.67	22.75	22.08	23.83	19.81	22.26	22.47
0.8	18.27	23.03	22.96	21.63	23.66	18.20	22.12	22.26
0.9	19.23	23.03	23.10	21.63	24.22	18.20	21.84	21.98
1.0	18.55	21.62	23.45	22.05	23.71	20.48	21.70	24.99
2.0	19.25	21.96	23.24	22.68	23.80	21.07	21.98	22.26
3.0	19.69	22.89	21.98	22.72	24.36	20.37	22.84	24.64
4.0	21.07	21.46	22.05	22.39	24.08	20.30	22.84	25.41
5.0	20.76	22.19	22.68	22.61	23.52	21.84	22.54	21.49
Check	18.62	21.98	20.93	22.12	22.75	21.84	21.41	20.09

\* On account of an accident no determinations were made at the end of 40 weeks.

An examination of table 8 shows results that closely approximate those obtained previously. No nitrogen is lost, so the nitrates are only changed to some other form of nitrogen.

Straw in large amounts causes a decrease in the formation of nitrates. The process of nitrification is probably not interfered with (it will be shown later that the cellulose of straw has no harmful effect on nitrate bacteria), but as fast as the nitrates are formed they are used by bacteria that obtain carbon from the straw. (That the number of bacteria increase with an increase in the amount of straw is shown in a subsequent portion of this paper.)

TABLE 9  
*Nitrate nitrogen per 100 gm. of soil—Average of two determinations*

AMOUNT OF STRAW	AT BEGINNING	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	52.93	47.88	50.96	52.76
0.2	52.93	48.58	51.24	52.62
0.3	52.93	49.66	52.71	51.92
0.4	52.93	49.28	51.38	50.80
0.5	52.93	49.42	51.38	53.34
0.6	52.93	49.14	47.88	53.20
0.7	52.93	42.98	50.12	52.04
0.8	52.93	40.70	48.72	53.76
0.9	52.93	41.58	47.18	52.36
1.0	52.93	43.54	46.06	49.00
2.0	52.93	37.94	46.43	46.48
3.0	52.93	37.66	45.78	44.38
4.0	52.93	29.26	46.06	43.40
5.0	52.93	30.24	47.18	42.84
Check	52.93	41.30	52.30	53.90

*The effect of straw on nitrates already in the soil*

In the foregoing study of the effect of straw on nitrification, the tests were made on the influence of straw in transforming an ammonium compound to nitrates. The question arises, what happens to nitrates already in the soil when straw is added? With this problem in view, 50 mgm. of nitrate nitrogen in the form of sodium nitrate was added to 100 gm. of soil, to which had been added the various percentages of straw. Nitrate analyses were made immediately and at the end of 6, 12 and 18 weeks. The results of the analyses are given in the tables 9, 10 and 11.

At the end of 6 weeks there was a loss in nitrates in all cases. There was less loss between 0.1 and 0.7 per cent straw than in the check. Above 1 per cent straw there is a very much greater loss than in the check.

There was a loss in nitrates in all cases at the end of the 12-week period. The loss in the case of the check was very small. In all except one there was a greater loss when straw had been added. In general, as the straw increased the loss increased.



At the end of the 24-week period there was a loss in nitrates in every case but in the check. The loss is greatest above 1 per cent straw.

TABLE 10

*Increase or decrease in nitrate nitrogen over the nitrate nitrogen in the beginning*

AMOUNT OF STRAW ADDED	END OF 6 WEEKS	END OF 18 WEEKS	END OF 18 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	-5.05	-1.97	-0.17
0.2	-4.35	-1.69	-0.31
0.3	-3.27	-0.22	-1.01
0.4	-3.65	-1.55	-2.13
0.5	-3.51	-1.55	0.41
0.6	-3.79	-5.05	0.27
0.7	-9.95	-2.81	-0.89
0.8	-12.23	-4.21	0.83
0.9	-10.35	-5.75	-0.57
1.0	-8.39	-6.87	-3.93
2.0	-14.99	-6.50	-6.45
3.0	-15.27	-7.15	-8.55
4.0	-23.67	-6.87	-9.53
5.0	-22.69	-5.75	-10.09
Check	-11.63	-0.59	1.03

TABLE 11

*Increase or decrease over the increase or decrease in nitrate nitrogen in the check at the different periods*

AMOUNT OF STRAW ADDED	END OF 6 WEEKS	END OF 12 WEEKS	END OF 18 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	6.58	-1.38	-1.20
0.2	7.28	-1.10	-1.34
0.3	8.36	0.37	-2.04
0.4	7.98	-0.96	-3.47
0.5	8.12	-0.96	-0.62
0.6	7.84	-4.46	-0.76
0.7	1.68	-2.22	-1.92
0.8	-1.60	-3.62	-0.20
0.9	1.28	-5.16	-1.60
1.0	2.24	-6.28	-4.96
2.0	-3.36	-5.91	-7.48
3.0	-3.64	-6.56	-9.58
4.0	-12.06	-6.28	-10.56
5.0	-11.06	-5.16	-11.12
Check			

It is evident that straw has an effect on nitrates present in the soil and as the amount of straw increases the harmful effect increases.

*The effect of straw on ammonification*

The various amounts of straw were added to 100 gm. of soil in tumblers. After the moisture had been adjusted 1 per cent casein was added to one set. The other set stood a week and then 1 per cent casein was added to it. After the addition of the casein the soil was incubated one week. Magnesium oxide and water were added to the 100 gm. of soil and the ammonia determined by distillation.

Practically all the bacteria in the soil are ammonifiers. Straw, as is shown in another part of the paper, stimulates bacterial reproduction. It was thought that if the soil stood some time with the straw, greater ammonification would take place as a result of the increase in the number of bacteria. It was with

TABLE 12  
*Ammonia per 100 gm. of soil—Average of two determinations*

AMOUNT OF STRAW	A. CASEIN APPLIED AT ONCE	B. CASEIN APPLIED 1 WEEK AFTER STRAW
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	128.27	129.55
0.2	126.14	124.10
0.3	122.82	132.34
0.4	125.89	118.49
0.5	124.10	126.48
0.6	113.24	126.91
0.7	126.99	127.50
0.8	117.81	125.29
0.9	117.97	126.65
1.0	110.16	111.27
2.0	98.52	89.41
3.0	81.36	98.10
4.0	79.31	94.95
5.0	70.13	68.68
Check—no straw	132.17	125.38
Check—no casein, no straw	5.44	3.32

this point in mind that the soil plus the various amounts of straw was allowed to stand a week before the addition of the casein. In table 12, column A, the ammonia formed in one week is recorded. Column B shows the ammonia formed in one week where the casein was applied one week after the addition of the straw.

It is evident that above 0.9 per cent straw a harmful effect is exerted upon the process of ammonification. As the straw increases the ammonia decreases. This is true in both cases. The figures in column B do not show the increased ammonification due to the increase in bacterial numbers. It is likely that as much ammonia is formed above 0.9 per cent straw, but since there are enormous numbers of bacteria using the straw as a source of carbon, they may use the ammonia as a source of nitrogen.

*The effect of straw on the fixation of atmospheric nitrogen*

In order to complete the study of the biological activities in which soil bacteria function, the writer next took up the effect of straw on the fixation

TABLE 13

*The effect of straw on nitrogen fixation; nitrogen 10 gm. of soil—Average of two determinations*

AMOUNT OF STRAW ADDED	AT BEGINNING	END OF 3 WEEKS	END OF 6 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	10.01	12.04	13.72
0.2	9.97	12.11	12.81
0.3	9.78	12.74	13.16
0.4	10.15	12.25	12.46
0.5	10.01	12.46	11.90
0.6	10.36	12.32	12.81
0.7	10.22	11.34	12.67
0.8	10.29	11.48	13.09
0.9	10.64	12.11	13.16
1.0	10.43	12.18	12.31
2.0	11.06	12.04	12.60
3.0	11.06	12.32	13.30
4.0	10.57	12.12	13.72
5.0	11.06	12.18	13.86
Check	10.57	11.13	13.24

TABLE 14

*Increase in nitrogen over the nitrogen in the beginning for the different periods*

AMOUNT OF STRAW ADDED	END OF 3 WEEKS	END OF 6 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	2.03	3.71
0.2	2.14	2.84
0.3	2.96	3.38
0.4	2.10	2.31
0.5	2.45	1.89
0.6	1.96	2.45
0.7	1.12	2.45
0.8	1.19	2.80
0.9	1.47	2.52
1.0	1.75	1.88
2.0	0.98	1.54
3.0	1.26	2.24
4.0	1.55	3.15
5.0	1.12	2.80
Check	0.56	1.77

of nitrogen over a period of 3 and 6 weeks. In one set of tests the different amounts of straw were added. Total-nitrogen determinations were made in duplicate immediately at the end of 3 and 6 weeks by the modified Gunning method. At the same time another series was conducted to which 1 per cent

of mannite had been applied in addition to the straw. From an analysis of tables 12, 13, 14 and 15, it is seen that straw serves as a source of carbon to nitrogen-fixing bacteria. In the case in which the mannite was added, more

TABLE 15

*The effect of straw on nitrogen fixation; nitrogen 10 gm. of soil; mannite added—Average of two determinations*

AMOUNT OF STRAW ADDED	AT BEGINNING	END OF 3 WEEKS	END OF 6 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	10.36	13.51	14.21
0.2	10.43	13.79	14.07
0.3	10.43	13.81	13.86
0.4	10.78	13.72	13.79
0.5	10.15	13.72	13.86
0.6	10.92	13.72	13.37
0.7	10.62	13.64	14.14
0.8	10.78	13.23	14.21
0.9	10.78	14.07	14.35
1.0	10.29	13.65	14.07
2.0	10.85	13.93	14.21
3.0	11.38	13.86	14.35
4.0	10.78	14.21	15.19
5.0	10.92	14.07	14.77
Check	10.85	13.30	14.14

TABLE 16

*Increase in nitrogen over the nitrogen in the beginning for the different periods; mannite added*

AMOUNT OF STRAW ADDED	END OF 3 WEEKS	END OF 6 WEEKS
<i>per cent</i>	<i>mgm.</i>	<i>mgm.</i>
0.1	3.15	3.86
0.2	3.36	3.64
0.3	3.38	3.43
0.4	2.94	3.01*
0.5	3.57	3.71
0.6	2.80	2.67*
0.7	3.02	3.52
0.8	2.45	3.43
0.9	3.29	3.57
1.0	3.36	3.78
2.0	3.08	3.36
3.0	2.48	2.97
4.0	3.43	4.41
5.0	3.15	3.75
Check	2.45	3.29

nitrogen was fixed, mannite being a very readily utilized source of carbon. In only three cases was there less nitrogen fixed than in the check. These are marked with an asterisk in the tables.

*The effect of straw on the number of bacteria in the soil*

In this test straw in the varying amounts was added to tumblers containing 100 gm. of soil each. After 3 weeks the bacteria were counted by the dilution-beef-agar-plate method. Thereafter the numbers of bacteria in the soil were counted at approximately 6-week intervals over a period of 71 weeks. The initial number of bacteria in the soil was 2,730,000 per gram.

From an examination of table 17 it is at once apparent that as the straw increases bacteria increase in numbers. This is especially noticeable above 1 per cent straw, where unheard-of numbers of bacteria were present. For example, at the end of 12 weeks the count with the 5 per cent straw lies between 130 and 190 million bacteria. At the end of the 71 weeks the count with the 4 per cent straw has fallen off to 67 million but the same general relationship holds even then. The bacterial counts for all the periods are averaged and the results graphically expressed in figure 1. In this diagram the ordinate represents the average number of bacteria for the whole period of the work. From the numbers given the last four ciphers have been omitted. The abscissa represents the percentage of straw added.

*The effect of straw on the types of bacteria present in the soil*

In order to find out whether straw stimulates or inhibits any particular group of bacteria, a study of the effect of straw on bacteria was carried out. About one year (53 weeks) after the soil had been inoculated with the various amounts of straw as described in the preceding section, the soil was plated for counting. All the colonies on a high-dilution plate, usually one on which there were between fifty and one hundred colonies, were picked and inoculated on agar slants. The following soil samples were used: 0.3 per cent, 0.6 per cent, 1 per cent and 4 per cent straw, and the check. Besides these, the writer made a study of the bacteriology of a fresh sample of straw and of soil. It is obviously impossible to study all the bacteria in a gram of soil, but this method gives an approximation of the flora.

The following culture media were used:

1. *Litmus milk*—Dehydrated litmus milk (Digestive Ferments Company), 29 gm. in 1000 cc. of distilled water.
2. *Beef bouillon*—1 per cent peptone, 0.5 per cent salt, 0.3 per cent Liebig's extract of beef, in distilled water. Reaction +1.5 per cent.
3. *Beef peptone agar*—Same as no. 2 with 1.5 per cent agar-agar.
4. *Gelatin*—Same as no. 2 with 10 per cent gelatin, reaction +1.5 per cent.
5. *Dextrose bouillon*—Same as no. 2 with 1 per cent dextrose, reaction neutral.
6. *Lactose bouillon*—Same as no. 2 with 1 per cent lactose, reaction neutral.
7. *Dunham's solution*—1 per cent peptone, 0.5 per cent salt in distilled water.
8. *Nitrate solution*—0.1 per cent peptone, 0.02 per cent  $\text{KNO}_3$ , in distilled water.

TABLE 17  
*Number of bacteria per gram of soil—last four cipters omitted*

AMOUNT OF STRAW	AFTER 3 WEEKS	AFTER 8 WEEKS	AFTER 13 WEEKS	AFTER 18 WEEKS	AFTER 24 WEEKS	AFTER 30 WEEKS	AFTER 36 WEEKS	AFTER 42 WEEKS	AFTER 48 WEEKS	AFTER 53 WEEKS	AFTER 60 WEEKS	AFTER 64 WEEKS	AFTER 71 WEEKS	AVERAGE
<i>per cent</i>														
0.1	276	300	196	472	97	200	230	200	73	170	174	234	190	216.3
0.2	365	500	150	249	293	130	191	371	310	500	570	534	256	339.9
0.3	351	1,000	322	395	530	355	138	490	97	550	480	335	390	418.0
0.4	546	1,900	346	359	690	260	404	800	550	560	310	710	300	565.0
0.5	700	5,000	700	359	510	820	416	640	84	800	330	860	420	895.3
0.6	900	2,400	1,300	595	670	685	404	950	131	1,200	570	1,350	590	903.4
0.7	900	2,700	1,100	700	637	610	760	660	140	750	500	1,030	560	849.7
0.8	3,100	2,000	1,400	700	1,320	1,240	137	1,440	270	1,150	590	1,340	520	1146.7
0.9	5,500	3,900	1,300	954	850	1,100	670	1,280	200	1,900	870	1,050	870	1572.6
1.0	3,200	4,000	800	900	1,920	1,210	1,540	1,470	200	1,700	1,070	1,240	1,800	1615.7
2.0	2,600	3,800	3,100	2,800	5,300	2,380	2,690	5,020	730	4,000	5,000	2,820	1,780	2824.2
3.0	13,800	11,300	7,900	3,000	8,200	4,500	3,500	5,500	490	6,300	2,900	5,000	6,100	6037.7
4.0	13,400	14,200	10,000	7,700	16,000	7,730	7,200	12,800	1,920	7,800	5,000	7,900	6,700	9104.0
5.0	13,700	13,300	19,200	14,600	17,800	5,200	7,800	8,000	1,310	5,700	3,800	8,300	4,300	9462.3
Check	326	222	111	230	166	190	66	196	40	150	94	290	100	167.7



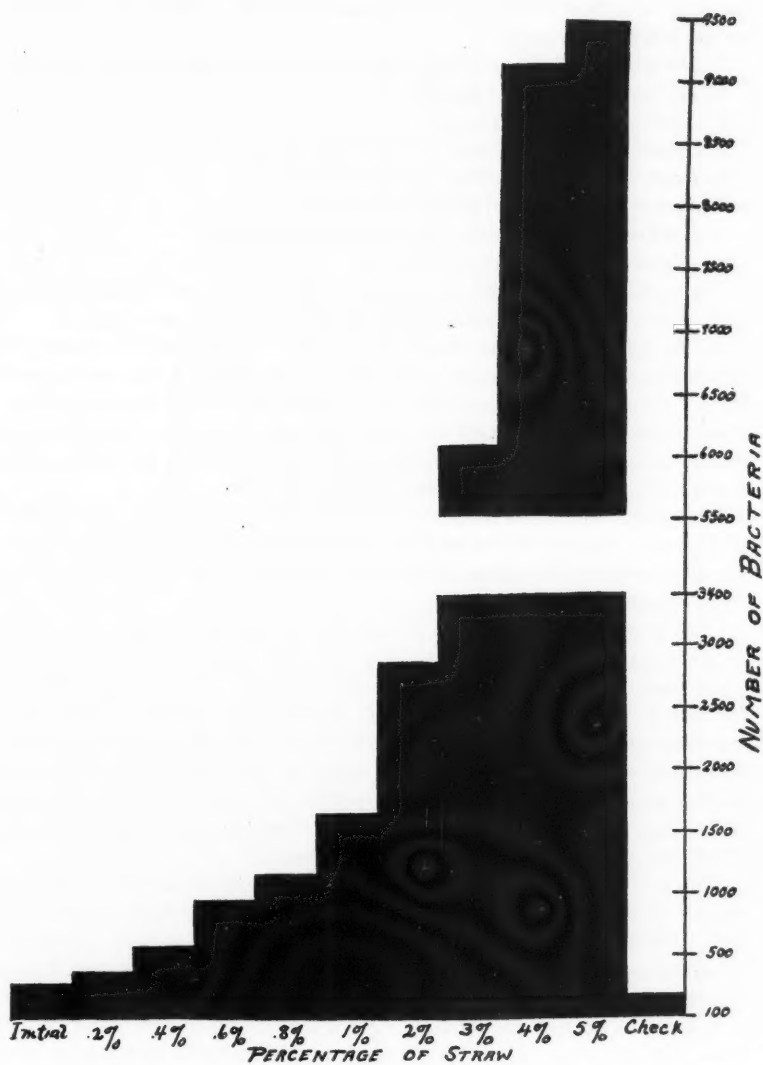


FIG. 1. DIAGRAM SHOWING NUMBERS OF BACTERIA IN SOILS VARIOUSLY TREATED

Media no. 5 and 6 were put in fermentation tubes. All media were sterilized in an autoclave 15 minutes, at 15 pounds pressure. The media were used for the following purposes:

1. *Litmus milk*—Acid and alkali production; casein coagulated or digested.
2. *Beef bouillon*—Type of growth.
3. *Agar slant*—Type of growth.
4. *Gelatin stab*—Type of liquefaction or type of growth.
5. *Dextrose bouillon*—Acid and gas production.
6. *Lactose bouillon*—Acid and gas production.
7. *Dunham's solution*—Indol and ammonia production.
8. *Nitrate solution*—Nitrite production.

The staining reactions and morphology of the bacteria were determined, as well as their physiological and cultural characters, on the above media.

In the tables giving the results the reaction in Dunham's solution are omitted because all the organisms studied formed ammonia and none formed indol. None of the bacteria formed gas in either dextrose or lactose bouillon. None of the organisms except sixteen in the sample of straw formed acid in lactose bouillon. These are marked with an asterisk in the table. The reactions in lactose bouillon are omitted from the tables.

The cultural and morphological characters were compared with descriptions in Chester's Manual of Determinate Bacteriology (2). As the descriptions are often meagre, the names assigned to bacteria in the tables are but an approximation.

From a study of tables 18 to 25 inclusive, it becomes apparent that the predominating type of bacteria in all cases is the gram positive, proteolytic, spore-bearing streptobacillus. In the field soil that had no storage 40.6 per cent are *B. subtilis* and 49.5 per cent *B. megatherium*, organisms which have the same general characters. Practically all the bacteria are gram positive, spore-bearing bacilli, as shown in the table 25. All the organisms down to *Bact. oxylactium* are of this type. In the straw there is a more varied picture. Only 27 per cent belong to the *B. subtilis* and *B. megatherium* groups, although 81 per cent of the bacteria are spore-bearing bacilli.

The straw does not seem to stimulate any group of bacteria. The *B. subtilis* type predominates in all cases and also in the check and in the field soil. There is no progressive increase or decrease in this type. Although straw stimulates bacterial reproduction, as was shown previously, it is a reproduction of the types already in the soil, and no special group is favored.

A large number of the bacteria formed nitrites from nitrates in culture tubes, 72.5 per cent with 0.3 per cent straw, 55.2 per cent with 0.6 per cent straw, 86.2 per cent with 1 per cent straw, 90 per cent with 4 per cent straw and 83 per cent with the check. It was thought that this might have some bearing on the problem. With the higher percentages of straw there are enormous numbers of bacteria, and they may form nitrites in the soil from the nitrates. With this in mind the various amounts of straw were added to

TABLE 18  
*Bacteria in 0.3 per cent straw treatment—40 cultures studied*

NUMBER	AGAR SLANT	GELATIN STAB	DEXTROSE BOUILLON	LITMUS MILK	BEEF TEA	NITRATE SOLUTION	GRAM STAIN AND MORPHOLOGY	NAME
15	Echinulate	+ Stratiform	acid —	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
12	Echinulate	+ Stratiform	—	Alkaline digested	Sediment	—	Gram +, spores streptobacillus	<i>B. subtilis</i>
6	Beaded	— Filiform	—	No change	Sediment	—	Gram +, spores bacillus	<i>B. gingivinus</i>
3	Beaded	— Filiform	+	Alkaline digested	Sediment	+	Gram +, spores bacillus	<i>B. gingivinus</i>
1	Beaded	+ Nailhead	—	Alkaline digested	Sediment	+	Gram +, spores bacillus	<i>B. megatherium</i>
1	Beaded	+ Stratiform	—	Alkaline digested	Sediment	—	Gram +, coccus	<i>M. radiatus</i>
1	Echinulate	+ Stratiform	—	Alkaline digested	Sediment	+	Gram +, coccus	<i>M. radiatus</i>
1	Echinulate	+ Stratiform	—	Alkaline digested	Sediment	—	Gram +, coccus	<i>M. radiatus</i>

TABLE 19  
*Bacteria in 0.6 per cent straw treatment—38 cultures studied*

NUMBER	AGAR SLANT	GELATIN STAB	DEXTRORSE BOUILLON	LITMUS MILK	BEEF TEA	NITRATE SOLUTION	GRAM STAIN AND MORPHOLOGY	NAME
19	Echinulate	+ Stratiform	acid	Alkaline digested	Sediment	<i>nitrites</i> +	Gram +, spores streptobacillus	<i>B. subtilis</i>
13	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
2	Beaded	- Filiform	-	No change	Sediment	-	Gram +, spores streptobacillus	<i>B. gingivinus</i>
2	Echinulate	- Filiform	+	Acid coagulated	Sediment	+	Gram +, spores streptobacillus	<i>B. punctiformis</i>
1	Beaded	- Filiform	-	No change	Sediment	-	Gram +, spores streptobacillus	<i>B. gingivinus</i>
1	Echinulate	- Growth on the surface	-	Alkaline digested	Sediment	-	Gram +, spores short bacillus	<i>B. stercus</i>

TABLE 20  
*Bacteria in 1.0 per cent straw treatment—65 cultures studied*

NUMBER	AGAR SLANT	GELATIN STAB	DEXTROSE BOUILLON	LITMUS MILK	BEEF TEA	NITRATE SOLUTION	GRAM STAIN AND MORPHOLOGY	NAME
			<i>acid</i>			<i>nitriles</i>		
43	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
7	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
1	Echinulate	+ Infundibulum	-	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
5	Beaded	- Filiform	+	No change	Sediment	+	Gram +, spores short bacillus	<i>B. stercus</i>
4	Echinulate	+ Stratiform	+	Acid coagulated	Sediment	+	Gram +, spores streptobacillus	<i>B. liodermos</i>
2	Echinulate	+ Stratiform	+	Alkaline digested	Sediment	+	Gram +, spores large plump bacillus	<i>B. verticillatum</i>
1	Filiform	- Filiform	+	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. ginglimus</i>
1	Beaded	+ Infundibulum	-	No change	No change	-	Gram +, spores streptobacillus	<i>B. megatherium</i>
1	Filiform pink	- Filiform	-	Alkaline digested	Sediment	+	Gram +, bacillus	

TABLE 21  
*Bacteria in 4 per cent straw treatment—98 cultures studied*

NUMBER	AGAR SLANT	GELATIN STAB	DEXTROSE BOUILLON	LITMUS MILK	BEEF TEA	NITRATE SOLUTION	GRAM STAIN AND MORPHOLOGY	NAME
			<i>acid</i>			<i>nitrates</i>		
71	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
6	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
8	Echinulate	+ Stratiform	-	No change	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
4	Echinulate	+ Stratiform	+	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
1	Echinulate	+ Stratiform	+	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
1	Echinulate	+ Stratiform	+	No change	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
1	Echinulate	+ Stratiform	-	No change	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
4	Echinulate	+ Stratiform	+	Acid	Sediment	+	Gram +, spores streptobacillus	<i>B. lioedermos</i>
1	Echinulate	+ Stratiform	+	Acid	Sediment	-	Gram +, spores streptobacillus	<i>B. lioedermos</i>
1	Filiform	- Filiform	-	Alkaline digested	Sediment	-	Gram +, short bacterium	



TABLE 22  
*Bacteria in check, no straw added—72 cultures studied*

NUMBER	AGAR SLANT	GELATIN STAB	DEXTRASE BOUILLON	LITMUS MILK	DEEP TEA	NITRATE SOLUTION	GRAM STAIN AND MORPHOLOGY	NAME
			acid			nitritus		
32	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
24	Echinulate	+ Stratiform	+	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
3	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
4	Echinulate	+ Stratiform	+	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
1	Echinulate	+ Stratiform	+	Acid coagulated	Sediment	-	Gram +, spores streptobacillus	<i>B. nodermos</i>
1	Filiform	+ Stratiform	-	Alkaline digested	Sediment	+	Gram +, drumstick spores, bacillus	<i>B. sublanatus</i>
1	Beaded	- Filiform	-	No change	Sediment	+	Gram +, spores short bacillus	<i>B. sicus</i>
1	Beaded	- Filiform	-	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. ginglimus</i>
3	Echinulate, yellow pigment	+ Stratiform	+	Acid coagulated	Sediment	-	Gram +, short bacterium	<i>Bact. oxylicium</i>
1	Echinulate	No growth	-	No change	Sediment	+	Gram +, coccus	<i>M. lactic</i>
1	Echinulate	+ Infundibulum	+	Acid coagulated	No change	-	Gram +, coccus	<i>M. coronatus</i>

TABLE 23  
*Bacteria in field soil—101 cultures studied*

NUMBER	AGAR SLANT	GELATIN STAB	DEXTROSE BOUTILLO	LITMUS MILK	BEEF TEA	NITRATE SOLUTION	GRAM STAIN AND MORPHOLOGY	NAME
			<i>acid</i>			<i>nitrites</i>		
21	Echinulate	+ Infundibulum	-	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. megatherium</i>
11	Echinulate	+ Infundibulum	+	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. megatherium</i>
15	Echinulate	+ Infundibulum	-	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. megatherium</i>
3	Echinulate	+ Infundibulum	+	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. megatherium</i>
16	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
4	Echinulate	+ Stratiform	+	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
19	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
2	Echinulate	+ Stratiform	+	Alkaline digested	Sediment	-	Gram -, spores streptobacillus	<i>B. subtilis</i>
4	Echinulate	+ Complete	-	Complete digestion	Sediment	-	Gram +, spores streptobacillus	<i>B. mesentericus</i>
2	Filiform	+ Stratiform	+	Acid	Sediment	+	Gram +, spores streptobacillus	<i>B. liodermos</i>
2	Filiform	- Filiform	+	Acid	Sediment	+	Gram +, spores streptobacillus	<i>B. punctiformis</i>
2	Echinulate	- Filiform	-	Alkaline	Sediment	+	Gram +, spores streptobacillus	<i>B. gingivinus</i>

TABLE 24  
*Bacteria in straw—86 cultures studied*

NUMBER	AGAR SLANT	GELATIN STAB	DEXTROSE BOUILLON	LITMUS MILK	BEEF TEA	NITRATE SOLUTION	GRAM STAIN AND MORPHOLOGY	NAME
			<i>acid</i>			<i>nitrates</i>		
19	Filiform	- Growth on surface	-	Alkaline digested	Film sediment	-	Gram +, spores short bacillus	<i>B. sicus</i>
12	Filiform	- Growth on surface	-	Alkaline digested	Film sediment	+	Gram +, spores short bacillus	<i>B. sicus</i>
8	Echinulate	+ Infundibulum	-	Complete digestion	Sediment	-	Gram +, spores streptobacillus	<i>B. subtilis</i>
6	Echinulate	+ Stratiform	-	Alkaline digested	Sediment	+	Gram +, spores streptobacillus	<i>B. subtilis</i>
9	Echinulate	+ Complete	-	Complete digestion	Film sediment	+	Gram +, spores streptobacillus	<i>B. megatherium</i>
7	Filiform	+ Infundibulum	+	Alkaline digested	Sediment	-	Gram +, spores short bacillus	<i>B. deltrudens</i>
10*	Filiform	+ Complete	+	Acid	Sediment	+	Gram +, short bac-terium	<i>Bact. lactis</i>
6*	Filiform	+ Infundibulum	+	Acid	Sediment	+	Gram +, coccus	<i>M. simplex</i>
5	Filiform	+ Infundibulum	+	Alkaline	Sediment	-	Gram +, coccus	<i>M. radiatus</i>
4	Echinulate	+ Stratiform	-	Alkaline	Sediment	+	Gram +, coccus	<i>M. radiatus</i>

\* Acid formed in lactose bouillon.

100-gm. samples of soil to which had been added 50 mgm. of nitrate nitrogen in the form of sodium nitrate. After a period of 1 and 2 weeks the soil was leached out with distilled water and the nitrites determined by the colorimetric method (9). Nitrites were not found present in any appreciable amounts in any case.

In no case was there a larger amount of nitrites found than in the check to which no straw had been added, and in the check to which no straw and no nitrate had been added. In many cases there were no nitrites present at all. The greatest amount of nitrite found was 0.1 mgm. per 100 gm. of soil. The nitrates that are used by these bacteria are evidently built up into organic nitrogen by the bacteria and are thrown off in the form of organic nitrogenous

TABLE 25  
Percentage of various bacteria

NAMES OF BACTERIA	0.3 PER CENT STRAW	0.6 PER CENT STRAW	1 PER CENT STRAW	4 PER CENT STRAW	CHECK, NO STRAW	FIELD SOIL	STRAW
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
<i>B. subtilis</i> .....	67.5	84.2	78.5	93.9	87.5	40.6	16.5
<i>B. megatherium</i> .....	2.5		1.5			49.5	10.5
<i>B. liodermos</i> .....			6.2	5.0	1.4		
<i>B. mesentericus</i> .....						4.0	
<i>B. sublanatus</i> .....					1.4		
<i>B. detrudens</i> .....							8.1
<i>B. verticillatum</i> .....			10.7				
<i>B. ginglimus</i> .....	22.5	7.9	1.5			2.0	
<i>B. punctiformis</i> .....		5.3				2.0	
<i>B. siccus</i> .....		2.6	7.7		1.4		36.0
<i>Bact. oxylicticum</i> .....					3.9		
<i>Bact. lactis</i> .....							11.6
<i>M. lactis</i> .....					1.4		
<i>M. coronatus</i> .....					1.4		
<i>M. simplex</i> .....							7.0
<i>M. radiatus</i> .....	7.5						10.5
Not identified.....			1.0	1.0			

material as a waste product. In the culture tubes, the media used contained only a trace of peptone and a small amount of nitrate. There was no source of carbon. In the soil, however the straw and other organic materials are present, so that the nitrate used by the bacteria is probably thrown off in an organic form.

*The effect of straw on the nitrate-forming bacteria in the soil*

In connection with this problem the question arises, has straw any effect on the nitrate bacteria? Does it inhibit their growth or development and consequently the formation of nitrates?

Eight strains of nitrate bacteria were isolated. The following liquid medium (4) in distilled water was used:  $\text{MgSO}_4$  0.04 per cent,  $\text{Fe}_2(\text{SO}_4)_3$  0.04 per cent,  $\text{NaCl}$  0.05 per cent,  $\text{K}_2\text{HPO}_4$  0.05 per cent,  $\text{Na}_2\text{CO}_3$  0.1 per cent,  $\text{NaNO}_2$  0.1 per cent. About 1 gm. of soil was inoculated into 500-cc. Erlenmeyer flasks containing about 150 cc. of the above sterile medium. The flasks were incubated at room temperature. They were tested for the presence of nitrates weekly. As soon as nitrates were found present, 1 cc. of the medium was transferred to some new medium. After four transfers were made 1 cc. of the medium was diluted and plated on nitrite agar. This medium was the same as given above, but for the addition of 2 per cent agar-agar (Difco). Colonies were picked from the plates and inoculated into the liquid medium again, which was tested for the presence of nitrates at intervals. If nitrates were found a pure culture of nitrate bacteria had been isolated.

In this work silica jelly, the original medium on which Winogradski isolated the nitrate bacteria, was tried but much better results were obtained when agar-agar (Difco) was used as a solidifying agent. A very interesting fact was noticed in the isolation work. The nitrate bacteria formed small indentations in the agar. The agar is probably softened by the nitric acid that is formed. One organism has been isolated that completely liquefies the agar medium after a few weeks. The area about the colonies of nitrate bacteria in the agar medium also is greatly softened.

The effect of cellulose was tried on the eight strains of nitrate bacteria, first, the cellulose in filter paper, and then the cellulose in straw.

A solution of hydrated cellulose from filter paper was made up as follows (8): To a mixture of 100 cc. of concentrated  $\text{H}_2\text{SO}_4$  and 60 cc. of water that had been cooled to  $60^\circ\text{C}$ ., was added 5 gm. of moist filter paper. The 3-litre flask containing the mixture was shaken until the paper dissolved, and was then completely filled with cold water. The cellulose was thrown out of solution in a finely divided mass, and after being allowed to settle, the supernatant fluid was poured off. More water was added and the process repeated until all the acid disappeared. The suspension of cellulose was then made up to any strength desired. The cellulose from the straw was made in the same manner.

Various amounts of the concentrated suspension of cellulose from filter paper and straw were placed in petri dishes so that the amounts ran from 0.1 to 1 per cent at intervals of tenths, and from 1 to 5 per cent at intervals of units. In the case of straw it was found impossible to make 4 and 5 per cent suspensions of cellulose with the medium. To all petri dishes was added 10 cc. of the nitrite agar mentioned before.

The nitrate bacteria were streaked over the surface of the agar and the growth examined after intervals. There was no harmful effect caused by the cellulose on the nitrate bacteria that could be noticed. In fact with the cellulose from the filter paper the growth seemed to increase with the con-

centration. With the cellulose from straw no difference in growth could be noticed. The results of this experiment indicate that cellulose itself has no harmful effect on nitrate-forming bacteria.

#### SUMMARY

1. The addition of straw has a harmful effect on nitrate accumulation in the soil after a given time.
2. As the amount of straw increases the harmful effect increases.
3. Total-nitrogen determinations throughout the work show that if there is a loss in nitrate nitrogen, it is transformed to some other form of nitrogen. It is not lost to the soil.
4. Straw has an effect on nitrates already in the soil. As the straw increases the loss in nitrates increases.
5. Straw acts as a source of energy for nitrogen-fixing bacteria. The amount of nitrogen fixed is not dependent upon the amount of straw.
6. The process of ammonification is inhibited above 0.9 per cent straw. As the straw increases the harmful effect increases.
7. Straw has a decided effect on the number of bacteria. As the straw increases the bacteria increase in numbers.
8. Straw has no effect on the kind of bacteria present in the soil. The same types of bacteria predominate in straw-treated soil as predominate in soil without straw.
9. Nitrates that are used by the bacteria are not given off in the nitrite form but probably as organic nitrogen.
10. Cellulose from either filter paper or straw has no effect on the nitrate-forming bacteria.

#### CONCLUSION

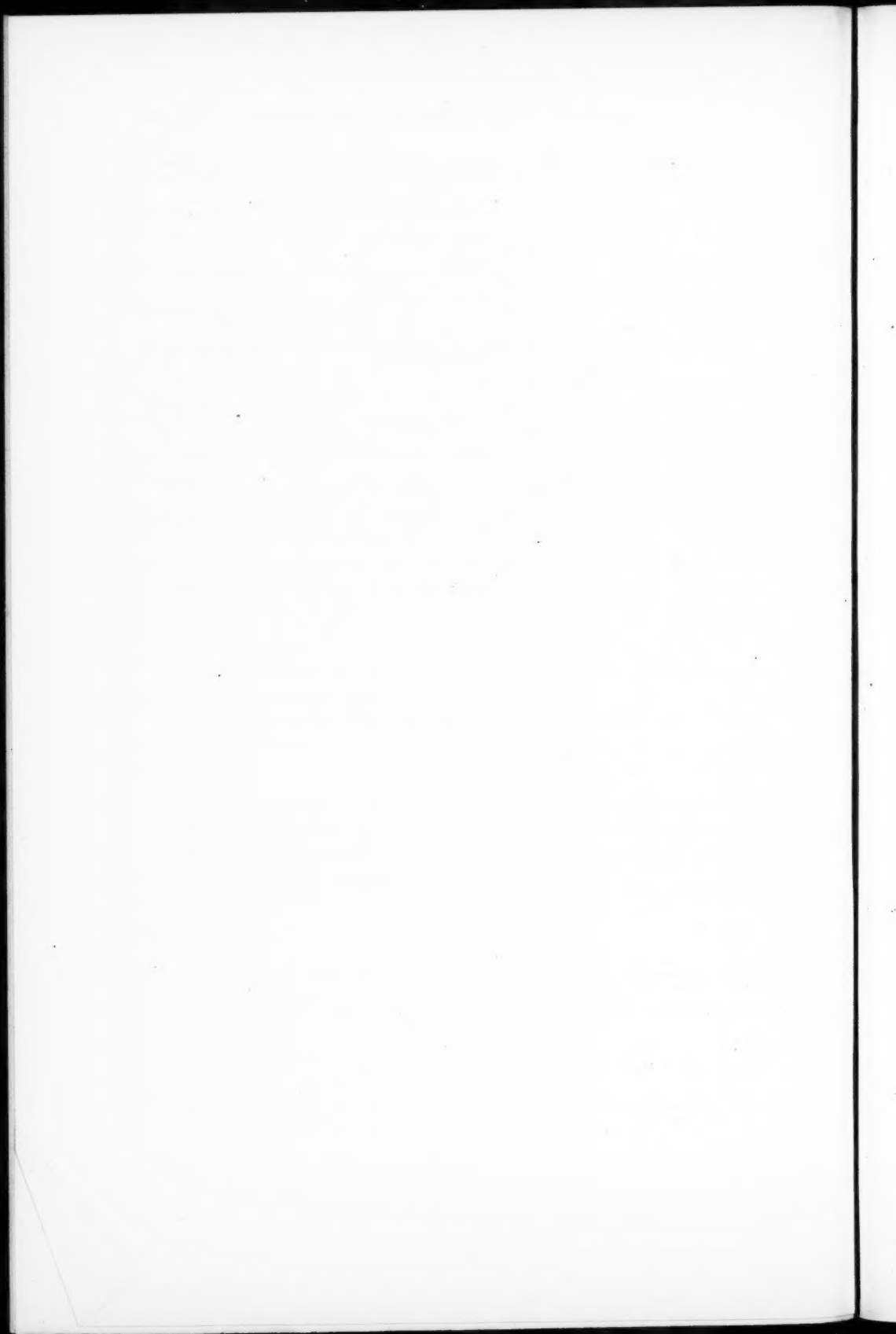
Straw applied to the soil stimulates the reproduction of bacteria. The bacteria use the straw as a source of carbon and use the nitrates (or in some cases ammonium sulfate) as a source of nitrogen. The nitrates are transformed to organic nitrogenous material and for the time being are lost as available plant-food. The intensity of the reaction depends upon the amount of straw.

#### REFERENCES

- (1) BISCHOFF, A. 1914 Straw as a fertilizer under various conditions. *In* Jour. Landw., Bd. 62, no. 1, p. 1-95; *abs. in* Exp. Sta. Rec., v. 31, p. 226.
- (2) CHESTER, F. D. 1903 A Manual of Determinative Bacteriology. MacMillan, New York.
- (3) CHIRIKOV, F. V., AND SHMUK, A. A. 1913 Experiments on denitrification. *In* Izv. Moscov. Selsk. Khoz. Inst. (Ann. Inst. Agron. Moscou), v. 19, p. 270-286; *abs. in* Exp. Sta. Rec., v. 29, p. 817.
- (4) DORYLAND, C. J. T. 1916 The influence of energy material upon the relation of soil microorganisms to soluble plant food. N. D. Agr. Exp. Sta. Bul. 116, p. 319-401.



- (5) HEINEMANN, P. G. 1905 A Laboratory Guide in Bacteriology, p. 39. Univ. Chicago.
- (6) HILL, HARRY H. 1912 The determination of nitrates in soils and soil extracts. *In* Va. Agr. Exp. Sta. Ann. Rpt. 1911-12, p. 133-144.
- (7) LÖHNIS, P., AND GREEN, H. H. 1914 The formation and decomposition of humus as well as its action on nitrogen assimilation. *In* Centbl. Bakt. (etc.), Abt. 2, Bd. 40, p. 52-60; *abs. in* Exp. Sta. Rec., v. 31, p. 120.
- (8) SCALES, F. M. 1915 A new method for precipitating cellulose for cellulose agar. *In* Centbl. Bakt. (etc.), Abt. 2, Bd. 44, p. 661-663.
- (9) SCHREINER, O., AND FAILEYER, G. H. 1906 Colorimetric, turbidity, and titration methods used in soil investigations. U. S. Dept. Agr. Bur. Soils Bul. 31.
- (10) STÖRMER, K. 1911 Experiments on the effect of straw on the action of the nitrogen of green manures. *In* Fühling's Landw. Ztg., Bd. 60, no. 6, p. 185-198; *abs. in* Exp. Sta. Rec., v. 25, p. 62.
- (11) STUTZER, A. 1907 Investigations on the action of heavy applications of ammonium sulphate in the presence of organic substances and calcium carbonate in the soil. *In* Jour. Landw., Bd. 55, no. 1, p. 81-91; *abs. in* Exp. Sta. Rec., v. 19, p. 220.
- (12) VON MAY, F. 1914 On the influence of straw on the availability of organically combined nitrogenous fertilizers. *In* Mitt. Landw. Lehrkranz. K. K. Hochsch. Bodenkul. Wein, Bd. 2, no. 3, p. 433-454; *abs. in* Exp. Sta. Rec., v. 31, p. 822.
- (13) VON SEELHORST, C., AND FRECKMANN, W. 1904 The influence of the depth of application of straw on the yield. *In* Jour. Landw., Bd. 52, no. 1-2, p. 163-171; *abs. in* Exp. Sta. Rec., v. 16, p. 33.
- (14) VON SEELHORST, C., AND FRECKMANN, W. 1904 Influence of applications of strawy manures on yield when used in conjunction with lime and sulphuric acid. *In* Jour. Landw., Bd. 52, no. 1-2, p. 172-174; *abs. in* Exp. Sta. Rec., v. 16, p. 33.



## THE SOLUBILITY OF ANIONS IN ALKALI SOILS<sup>1</sup>

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### INTRODUCTION

Cameron and Patten (4) showed in 1906 that sodium chloride is more easily removed from soils by leaching than sodium carbonate. Their studies were made with a fine sandy loam and a silty loam soil, each of which contained considerable amounts of the sulfate, chloride and carbonate of sodium. Columns of soil were leached under constant water pressure for a period of several weeks. The volume of water that passed through the soil and its content of chloride, carbonate and bicarbonate were determined at successive intervals.

The chloride was completely removed from each soil within a few weeks. Normal carbonate also disappeared, although much more slowly than the chloride, while small amounts of bicarbonate were still present in the percolates at the close of the experiment.

In preliminary leaching experiments with a light sandy soil that contained excessive amounts of various sodium salts, we have found that both the chloride and sulfate may be readily leached out, but appreciable amounts of soluble carbonate remained in the soil after prolonged leaching.

Vinson and Catlin (14), Hare (7) and Pittman (12) have shown that increasing amounts of carbonate are dissolved when alkali soils are extracted with increasing proportions of water. As pointed out by them, the ratio of soil to water used by the different chemical laboratories to extract the salts from alkali soils, varies from 1:2 to 1:20. The soil and water are also allowed to remain in contact, usually with periodic shaking, for different lengths of time, varying from 20 minutes to 24 hours.

It is well known that certain alkali soils may be substantially improved by drainage, especially when the drainage is followed by flooding or heavy irrigation. By this means barren alkali wastes, in certain localities, have been transformed into highly productive soil. On the other hand, drainage, even when accompanied by heavy flooding, has not proved to be an adequate means of reclaiming certain tracts of black-alkali soil in California (15) and other states (6).

<sup>1</sup> Paper No. 78, University of California, Graduate School of Tropical Agriculture and Citrus Experiment Station, Riverside, California.

From these and other references that could be cited, it seems that alkaline salts produce effects on soils, different either in kind or degree, from those produced by neutral salts. As is well known, the claim has frequently been made that alkaline salts are adsorbed by soil to a greater degree than neutral salts.

Despite the many investigations that have been made on alkali soils by the Bureau of Soils, Hilgard and various other workers, much still remains to be determined. It is desirable that we extend our knowledge concerning the mutual relationships that exist between soluble salts and soils.

In a previous paper from this laboratory (10) we have discussed some of the chemical effects that are produced when salts are added to soils. The present paper will deal mainly with the solubility of sodium salts as they occur in natural alkali soils. We have investigated (a) the effect of time on the extraction of salts, (b) the effect of different ratios of soil to water, and (c) the rate of solution of the several anions present in three types of alkali soil.

#### METHODS

Samples of air-dried soil were used that had been thoroughly mixed and passed through a 2-mm. screen. The extracts were made by shaking, with a mechanical shaker, portions of soil with distilled water from which all but traces of carbon dioxide had been removed by aeration. The extracts were filtered through Pasteur-Chamberland tubes with the aid of compressed air. The first portion of the filtrate, usually about 200 cc., was always discarded.

Carbonate and bicarbonate were determined as soon after filtration as possible by double titration with 0.05 *N* H<sub>2</sub>SO<sub>4</sub>, phenolphthalein and methyl orange being used as indicators. The pH values of the extracts were determined colorimetrically, with Clark and Lubs indicators and buffer solutions. Chloride was determined volumetrically by the Mohr method and sulfate gravimetrically, after first removing the silica. Nitrate was determined by reduction with aluminum in those extracts which contained appreciable amounts of chloride or dissolved organic matter. Otherwise, the nitrate was determined by the phenoldisulfonic acid method. Total soluble solids were determined by evaporating 100 cc. to dryness and heating the residue for an hour in an oven at 110°C.

The soluble constituents of the soils used in this investigation are composed mainly of sodium salts, but the content of chloride, sulfate, nitrate and soluble carbonate varies considerably. Sample 905 is a light sandy soil from Riverside, California; no. 907 is a sandy loam from Edison, California; and no. 908 is a fine sandy loam from Fresno, California. Soils 905 and 907 contain large amounts of CaCO<sub>3</sub>, while soil 908 is almost free from CaCO<sub>3</sub>.

EFFECT OF CO<sub>2</sub> IN THE COMPRESSED AIR

Since compressed air is commonly used in filtering soil extracts, it is desirable to determine whether compressed air produces any important effect on the carbonate content of the extract. It seemed possible that the carbon-dioxide content of the compressed air might convert a portion of the dissolved carbonate into bicarbonate.

Duplicate portions of several different soils, each of which contained considerable amounts of soluble carbonate, were shaken an hour with aerated water in the ratio of 1:5. One solution of each soil was filtered with the aid of compressed air in the usual way. The other portion was simultaneously filtered with the same kind of filtering apparatus, suction being used instead of compressed air. In this case, the upper end of the filtering chamber, instead of being attached to the compressed-air line, was connected with a tube filled with soda lime to protect the extract from external CO<sub>2</sub>, the lower end of the filter being connected with a suction flask.

Analysis of the extracts showed that in no case was the content of normal carbonate reduced by filtering under pressure. On the contrary, the extracts from certain soils were found to contain slightly higher amounts of carbonate and correspondingly smaller amounts of bicarbonate, when filtered by means of compressed air, than when filtered by means of suction.

It is well known that equilibrium may be affected by pressure and temperature, and that the equilibrium between carbonate and bicarbonate is easily disturbed (3). It is possible that increasing the pressure tends to force the equilibrium of alkali soil extracts in the direction of increased amounts of CO<sub>3</sub>. From these results it seems safe to conclude, however, that the carbon dioxide contained in ordinary compressed air does not affect the content of normal carbonate in soil extracts to any great extent.

## EFFECT OF TIME ON THE SOLUBILITY

Portions of each soil were shaken with aerated water in the ratio of 1:5 for periods ranging from 5 minutes to 8 hours. The solutions were filtered immediately and analyzed. The average results of duplicate determinations are submitted in tables 1, 2 and 3.

The data show that soil 905 contains approximately 1.15 per cent total soluble matter; soil 907 contains slightly less than 0.20 per cent, and soil 908 contains approximately 2.50 per cent.

Similar results were obtained with each soil, so far as the effect of the time of shaking is concerned. The amount of total solids dissolved by shaking for 5 minutes was less than was dissolved by shaking for longer periods, but the solubility of no single ion was consistently increased in the same way.

These results indicate that constant shaking for a period of 1 hour affords sufficient time for approximate equilibrium to be established between water

and these soils. It seems probable that the variations in the lengths of time employed by the different laboratories in the extraction of alkali salts is a matter of no very great practical importance.

TABLE 1  
*Effect of time of shaking on the solubility of soil 905*

	TIME OF SHAKING				
	5 minutes	30 minutes	1 hour	4 hours	8 hours
Carbonate (CO <sub>3</sub> ) (p.p.m.).....	135	172	176	202	198
Bicarbonate (HCO <sub>3</sub> ) (p.p.m.).....	263	232	247	262	385
Chloride (Cl) (p.p.m.).....	2,244	2,249	2,293	2,251	2,256
Sulfate (SO <sub>4</sub> ) (p.p.m.).....	4,194	4,202	4,209	4,235	4,237
Nitrate (NO <sub>3</sub> ) (p.p.m.).....	326	321	321	332	332
Total soluble solids (p.p.m.).....	11,065	11,392	11,577	11,650	11,782
pH value.....	9.0	9.2	8.7	9.0	9.0

TABLE 2  
*Effect of time of shaking on the solubility of soil 907*

	TIME OF SHAKING				
	5 minutes	30 minutes	1 hour	4 hours	8 hours
Carbonate (CO <sub>3</sub> ) (p.p.m.).....	75	90	67	63	93
Bicarbonate (HCO <sub>3</sub> ) (p.p.m.).....	412	427	468	472	453
Chloride (Cl) (p.p.m.).....	37	37	36	37	36
Sulfate (SO <sub>4</sub> ) (p.p.m.).....	237	282	276	303	307
Nitrate (NO <sub>3</sub> ) (p.p.m.).....	27	28	28	28	29
Total soluble solids (p.p.m.).....	1,465	1,702	1,705	1,745	1,865
pH value.....	8.5	8.5	8.4	8.4	8.5

TABLE 3  
*Effect of time of shaking on the solubility of soil 908*

	TIME OF SHAKING				
	5 minutes	30 minutes	1 hour	4 hours	8 hours
Carbonate (CO <sub>3</sub> )* (p.p.m.).....	2,853	2,868	2,820	2,880	2,868
Chloride (Cl) (p.p.m.).....	7,601	7,694	7,889	7,783	7,800
Sulfate (SO <sub>4</sub> ) (p.p.m.).....	1,672	1,663	1,647	1,658	1,672
Nitrate (NO <sub>3</sub> ) (p.p.m.).....	1,271	1,348	1,425	1,387	1,371
Total soluble solids (p.p.m.).....	25,490	25,487	27,002	26,552	26,477
pH value.....	9.8+	9.8+	9.8+	9.8+	9.8+

\* Bicarbonate (HCO<sub>3</sub>) was not determined because of the dark color of the extracts.



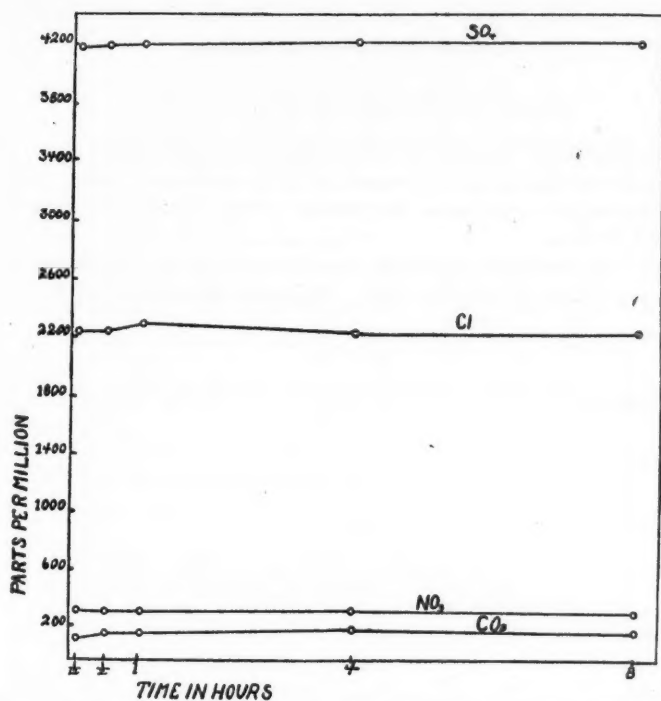


FIG. 1. EFFECT OF TIME OF SHAKING ON THE EXTRACTION OF ANIONS IN SOIL 905

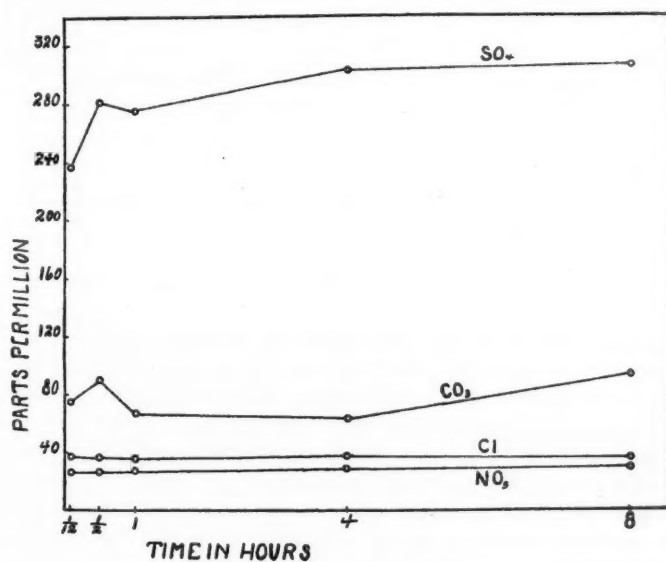


FIG. 2. EFFECT OF TIME OF SHAKING ON THE EXTRACTION OF ANIONS IN SOIL 907

## EFFECT OF THE RATIO OF SOIL TO WATER

In this experiment the ratio of soil to water was varied from 1:2 to 1:80. The soil, after adding the desired amount of water, was shaken 1 hour. Duplicate determinations were made, the average results of which are submitted in tables 4, 5 and 6.

The amounts of chloride and nitrate found were reasonably uniform throughout the entire range of dilutions used. With soils 905 and 907 the amounts

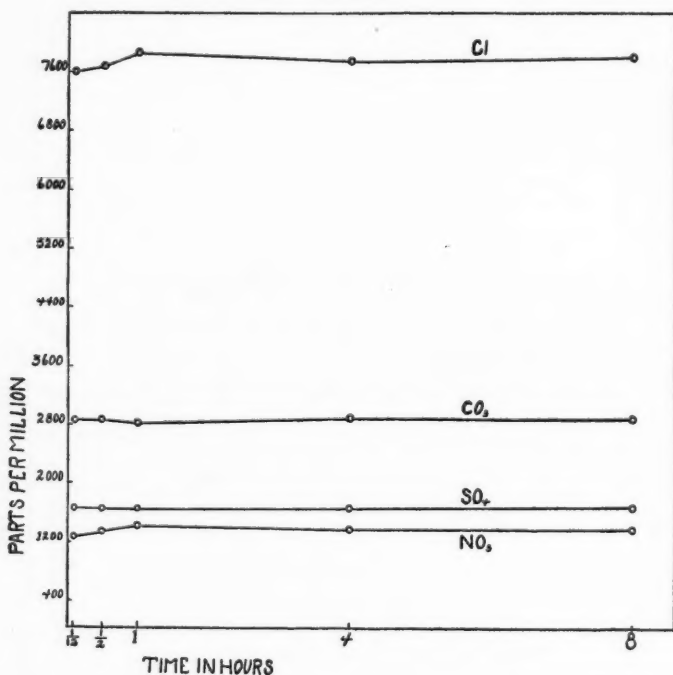


FIG. 3. EFFECT OF TIME OF SHAKING ON THE EXTRACTION OF ANIONS IN SOIL 908

of sulfate and total solids that were dissolved, advanced with increases in the proportions of water used, while with soil 908 no differences were found.

On the other hand, the data show at once that the total amounts of carbonate and bicarbonate extractable from soils 905 and 907 depend on the proportion of soil to water used. With soil 905 the amounts of carbonate and bicarbonate advanced with each increase in the proportion of water used. With soil 907 the amount of bicarbonate also increased in a similar manner, but the maximum amount of normal carbonate was recovered by the use of the ratio of 1:40.

TABLE 4

*Effect of different ratios of soil to water on the solubility of soil 905*

	RATIO OF SOIL TO WATER					
	1:2	1:5	1:10	1:20	1:40	1:80
Carbonate (CO <sub>3</sub> ) (p.p.m.).....	73	172	292	510	780	1,080
Bicarbonate (HCO <sub>3</sub> ) (p.p.m.).....	190	247	388	610	793	1,464
Total CO <sub>3</sub> * (p.p.m.).....	260	415	673	1,110	1,560	2,519
Chloride (Cl) (p.p.m.).....	2,300	2,293	2,287	2,296	2,305	2,553
Sulfate (SO <sub>4</sub> ) (p.p.m.).....	4,048	4,209	4,249	4,299	4,389	4,751
Nitrate (NO <sub>3</sub> ) (p.p.m.).....	319	321	310	354	319	312
Total soluble solids (p.p.m.).....	11,185	11,577	12,165	13,220	14,440	16,720
pH value.....	8.3	8.7	9.2	9.2	9.2	8.6

\* Calculated from the methyl orange titration.

TABLE 5

*Effect of different ratios of soil to water on the solubility of soil 907*

	RATIO OF SOIL TO WATER					
	1:2	1:5	1:10	1:20	1:40	1:80
Carbonate (CO <sub>3</sub> ) (p.p.m.).....	9	67	180	360	480	360
Bicarbonate (HCO <sub>3</sub> ) (p.p.m.).....	294	468	640	732	976	1,830
Total CO <sub>3</sub> * (p.p.m.).....	298	527	809	1,080	1,439	2,159
Chloride (Cl) (p.p.m.).....	41	36	35	35	35	35
Sulfate (SO <sub>4</sub> ) (p.p.m.).....	264	276	289	277	279	361
Nitrate (NO <sub>3</sub> ) (p.p.m.).....	28	28	29	32	34	28
Total soluble solids (p.p.m.).....	1,161	1,705	2,225	2,550	3,140	3,800
pH value.....	8.0	8.4	8.8	9.3	9.4	8.6

\* Calculated from the methyl orange titration.

TABLE 6

*Effect of different ratios of soil to water on the solubility of soil 908*

	RATIO OF SOIL TO WATER					
	1:2	1:5	1:10	1:20	1:40	1:80
Carbonate (CO <sub>3</sub> ) (p.p.m.).....	2,976	2,820	2,872	2,805	2,820	2,880
Bicarbonate (HCO <sub>3</sub> ) (p.p.m.).....						4,392
Chloride (Cl) (p.p.m.).....	7,772	7,889	7,951	8,139	7,960	7,943
Sulfate (SO <sub>4</sub> ) (p.p.m.).....	1,708	1,647		1,696	1,637	1,657
Nitrate (NO <sub>3</sub> ) (p.p.m.).....	1,506	1,425	1,457	1,484	1,488	1,488
Total soluble solids (p.p.m.).....	26,926	27,002	26,015	28,560	27,820	26,640
pH value.....	9.8+	9.8+	9.8+	9.8+	9.8+	9.4+

While bicarbonate was not determined in the extracts from soil 908 on account of the large amount of dissolved organic matter which they contained, it is nevertheless interesting to note that the amount of normal carbonate found was approximately the same with every ratio of soil to water that was used.

As is well known, ordinary distilled water contains more or less dissolved  $\text{CO}_2$ , but the amount is subject to considerable variation. In order to eliminate variation as far as possible, we, as stated above, have used distilled water which was as nearly free from  $\text{CO}_2$  as practicable. It is of interest to note in this connection that the  $\text{CO}_2$  content of other extracts of soil 905 have been found to be approximately the same, whether the solutions were made

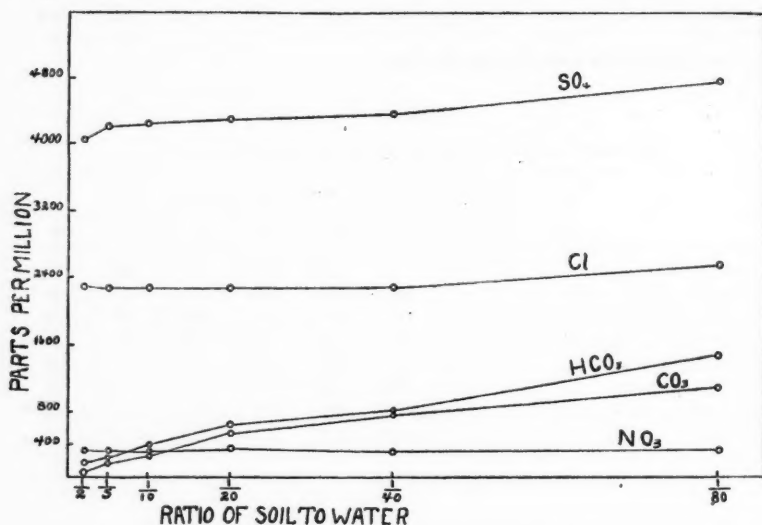


FIG. 4. EFFECT OF VARIOUS RATIOS OF SOIL TO WATER ON THE EXTRACTION OF ANIONS IN SOIL 905

with ordinary distilled water or with aerated water, but that the  $\text{HCO}_3$  content was appreciably higher when ordinary distilled water was used. This seems to indicate that the solid phase from which the dissolved carbonate was derived was not exhausted by the amount of aerated water used.

Equilibrium between  $\text{CO}_2$  and  $\text{HCO}_3$  is readily disturbed by changes in the temperature, by variations in the concentration of other salts, and perhaps most of all by the presence of dissolved  $\text{CO}_2$ . Moreover, aqueous solutions prepared by dissolving either  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  always contain both  $\text{CO}_3$  and  $\text{HCO}_3$  ions when equilibrium is established (3). For these reasons we have calculated the total  $\text{CO}_3$  from the methyl-orange titrations. The results indicate that the solid phase from which the  $\text{CO}_3$  and  $\text{HCO}_3$  were derived was

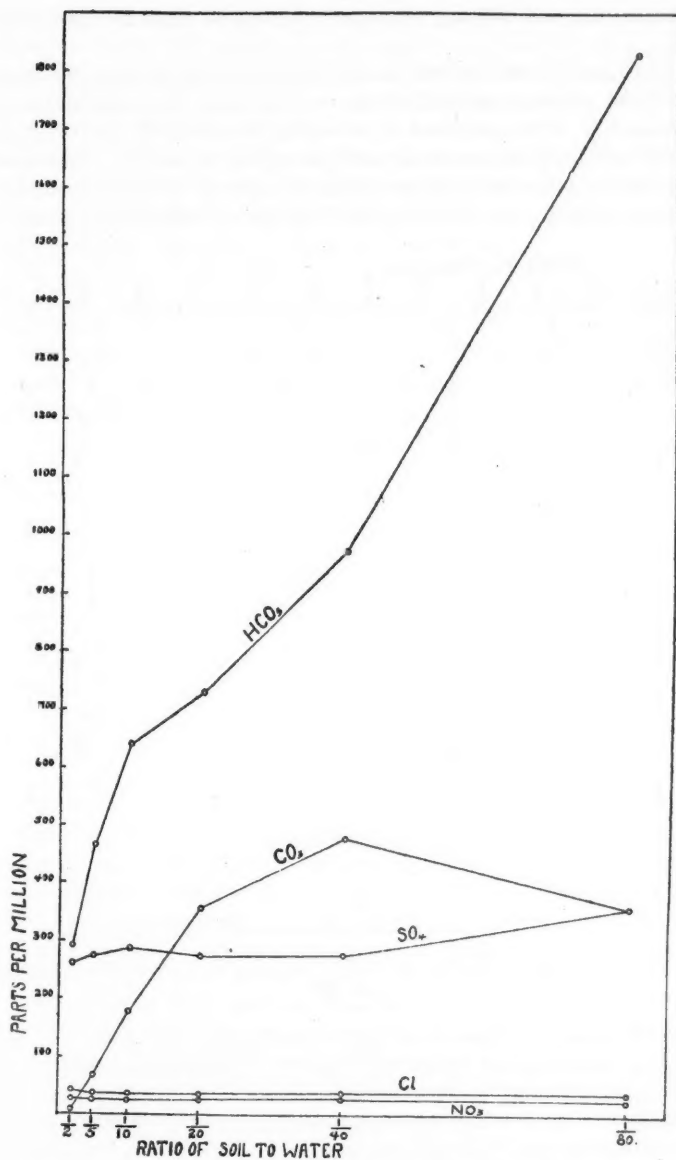


FIG. 5. EFFECT OF VARIOUS RATIOS OF SOIL TO WATER ON THE EXTRACTION OF ANIONS IN SOIL 907

not exhausted in soils 905 and 907, even by using 80 times as much water as soil.

The fact that soils 905 and 907 contain relatively large amounts of  $\text{CaCO}_3$ , while soil 908 contains practically none, must be taken into consideration in this connection. When expressed on the basis of air-dried soil, the 1:2 extract of soil 905 was found to contain 26 parts per million of calcium. With each increase in the proportion of water above the ratio of 1:2, greater absolute amounts of calcium were dissolved, the 1:80 extract having been found to

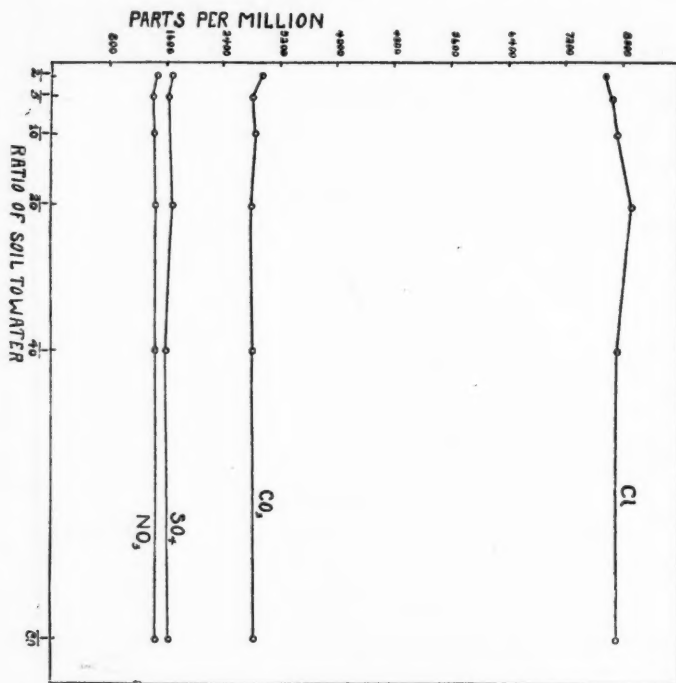


FIG. 6. EFFECT OF VARIOUS RATIOS OF SOIL TO WATER ON THE EXTRACTION OF ANIONS IN SOIL 908

contain 528 parts per million of calcium. The absolute amount of dissolved magnesium also increased with dilution, but to a lesser degree than that of calcium. On the other hand, the total amount of dissolved calcium and magnesium was by no means sufficient to satisfy the  $\text{CO}_3$  and  $\text{HCO}_3$  content of any of the extracts. In fact, the amount of sodium which passed into solution from adsorbed substances, or more probably from compounds of low solubility, increased with dilution very much more rapidly than was the case with calcium and magnesium. Since  $\text{CaCO}_3$  is appreciably soluble in

water and very much more so in solutions of neutral salts, and in view of the amounts of dissolved calcium, it is reasonably certain that a part of the  $\text{CO}_3$  and  $\text{HCO}_3$  found in the extracts of soils 905 and 907 was derived from  $\text{CaCO}_3$ , but it is certain that a still larger part of the dissolved  $\text{CO}_3$  and  $\text{HCO}_3$  was derived from sodium compounds.

The OH-ion concentration of the extracts is especially interesting. It will be noted that within certain limits of dilution, soils 905 and 907 gave extracts the pH value of which increased (denoting increasing OH-ion concentrations) as the proportion of water to soil increased.

With soil 905 the pH value of the extracts increased from 8.3 to 9.2 as the proportion of water was increased from 1:2 to 1:10, and further dilution up to 1:40 gave solutions of the same pH value as the 1:10 solution.

The 1:2 extract of soil 907 gave a pH value of 8.0 and each increase in the proportion of water, until the ratio of 1:40 was reached, gave extracts with increasing OH-ion concentration. With this dilution the pH value was 9.4.

TABLE 7  
*The concentration of  $\text{CO}_3$  and  $\text{HCO}_3$  in soil extracts*

	RATIO OF SOIL TO WATER					
	1:2	1:5	1:10	1:20	1:40	1:80
	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.	p. p. m.
Soil 905:						
$\text{CO}_3$ .....	36.5	34.0	29.0	25.5	19.5	13.5
$\text{HCO}_3$ .....	95.0	49.0	39.0	30.5	20.0	18.0
Soil 907:						
$\text{CO}_3$ .....	4.5	13.0	18.0	18.0	12.0	4.5
$\text{HCO}_3$ .....	147.0	94.0	64.0	37.0	24.0	23.0
Soil 908:						
$\text{CO}_3$ .....	1488.0	564.0	287.0	140.0	70.5	36.0

The extracts of soil 908 obtained by the use of ratios ranging from 1:2 to 1:40 each gave a pH value of 9.8 or more, which is the upper limit of the standard buffer solutions at our disposal. The 1:80 extract, however, was less alkaline, having a pH value of 9.4. In view of the fact that this soil contains relatively large amounts of sodium carbonate, it is not surprising that the OH-ion concentration of each of its extracts was high.

The preceding data were calculated as parts per million of the air-dried soil. In making the determinations it was noted, in the case of one soil, that the solutions obtained with the use of relatively small proportions of water actually contained less normal carbonate per unit volume than the 1:20 extract. To bring out the effects of dilution more clearly, the content of  $\text{CO}_3$  and  $\text{HCO}_3$  expressed as parts per million of the extract is submitted in table 7.

It will be noted that the 1:2 and 1:5 extracts of soil 905 contained approximately equal concentrations of  $\text{CO}_3$ . With each succeeding increase in the



relative proportions of water above 1:5, the extracts contained somewhat lower concentrations of  $\text{CO}_3$ , but the decreases were not proportional to the increases in the amount of water used. With soil 907 the concentration of  $\text{CO}_3$  in the extracts increased substantially as the proportion of water was increased, reaching its maximum with the ratios of 1:10 and 1:20. On the other hand, soil 908 gave extracts whose content of  $\text{CO}_3$  was approximately inversely proportional to the amount of water used.

The  $\text{HCO}_3$  content of the extracts of soils 905 and 907 was found to decrease as the proportion of water was increased, but in view of the variation in  $\text{CO}_3$  already noted the ratio of  $\text{CO}_3$  to  $\text{HCO}_3$  must have varied.

These data are in harmony with the results of Cameron and Briggs (3) in showing that the equilibrium between  $\text{CO}_3$  and  $\text{HCO}_3$  is affected by concentration. But, as suggested above, shifts in the equilibrium may also take place as a result of changes in the temperature and the partial pressure of  $\text{CO}_2$ . As the temperature is increased, or as the partial pressure of  $\text{CO}_2$  is decreased, the relative proportion of  $\text{CO}_3$  will increase.

Since the concentration of salts in alkali soils is subject to wide fluctuation as a result of irrigation, rains and evaporation, and the temperature of the soil and air varies many degrees within a single 24-hour period, and since the amount of  $\text{CO}_2$  is also subject to change, it seems questionable whether there is anything to be gained by making a distinction between  $\text{CO}_3$  and  $\text{HCO}_3$  in the ordinary analysis of alkali soils. Further discussion on this point will be submitted elsewhere.

It is quite evident from the preceding data that the amount of soluble carbonate and bicarbonate that will be found in a black-alkali soil may be influenced considerably by the ratio of soil to water used in making the extract. With certain soils the wider the ratio the greater will be the total amount found, while with other soils this does not seem to be true.

The preceding data indicate that the  $\text{OH}$ -ion concentration of an alkali soil, when determined in an aqueous extract or suspension of the soil, may, in some cases at least, be very different from that of the soil solution as it occurs in the open field. Under such conditions the  $\text{OH}$ -ion concentration may not be above the toxic limit for plant growth (8), although the soil may actually contain appreciable amounts of sodium carbonate.

The occurrence of  $\text{OH}$ -ions in excess of  $\text{H}$ -ions in the soil moisture is mainly due to the hydrolysis of salts of strong bases and weak acids. The preceding data indicate that both the hydrolysis and the solubility of sodium carbonate in soil 907 are dependent, to a considerable extent, on the proportion of soil to water; that is, on the total concentration of the solution at equilibrium with the solid phase.

Not only is the occurrence of excessive alkalinity in the soil solution due to hydrolysis, mainly of carbonates, but the actual concentration of  $\text{OH}$  ions at a given instant is dependent on the partial pressure of carbon dioxide in the soil atmosphere. Since the latter probably varies from time to time, depend-

ing on the amount furnished by growing plants and the variable activity of the micro-organisms present, the OH-ion concentration must vary also.

While a determination of the pH value of a soil suspension or extract, as an isolated soil factor, seems to be of doubtful value, practically every student of the alkali problem has placed emphasis on the question of the total amount of sodium carbonate present.<sup>2</sup> The preceding data show, however, that the usual methods do not give a true measure of the total amount present. In a subsequent paper, other methods for the determination of black alkali and the importance of carbon dioxide as a neutralizing agent in alkali soils, will be discussed.

#### RATE OF SOLUTION OF ANIONS IN ALKALI SOILS

As a means of securing further light on the solubility of the different constituents of these soils, portions of each were extracted with water several times. The procedure adopted was as follows.

Weighed amounts of soil were placed in clean acid bottles and sufficient water was added to effect three different ratios of soil to water. After shaking for 1 hour the solutions were filtered through Pasteur-Chamberland filters, care being taken to transfer as much of the soil as possible to the filter chamber.

The filtration was continued until all of the free water had been forced through the filter tube. The remaining soil was removed from the filtering apparatus by the aid of a spatula and re-introduced into the original bottle. A second quantity of water was added, sufficient in amount to effect the same ratio as before, and the contents were shaken for 1 hour and filtered. This process was repeated twice with soils 905 and 907 and three times with soil 908. The successive filtrates were analyzed with the results shown in tables 8, 9 and 10.

It will be noted that when soil 905 was extracted a second time with water in the ratio of 1:2 or 1:5, solutions were obtained which contained as much  $\text{CO}_3$  and  $\text{HCO}_3$  as the first extracts. With those ratios both the second and third extracts of soil 907 contained greater amounts of  $\text{CO}_3$  than the first, while the second extraction with the 1:10 ratio yielded as much  $\text{CO}_3$  as the first.

In contrast to soils 905 and 907, a relatively large proportion of the  $\text{CO}_3$  in soil 908 was dissolved by the first extraction. It is interesting to note, however, that appreciable amounts of soluble  $\text{CO}_3$  still remained in this soil after it had been extracted three times. In other words, the absolute amount of sodium carbonate that remained undissolved after the first extraction was appreciable in each of these soils, although not very great in any one of them.

<sup>2</sup> It is well known that successful crops may sometimes be grown on soils that contain several hundred parts per million of soluble  $\text{CO}_3$ . The pH value of a suspension of such soils is frequently above 9.0, but owing to adsorption and the action of  $\text{CO}_2$ , the soil films that are in contact with the roots of the growing plants probably contain much lower OH-ion concentration than the soil mass as a whole.

TABLE 8  
*Constituents dissolved from soil 905 by successive extraction*

	RATIO OF SOIL TO WATER								
	1:2			1:5			1:10		
	First extraction	Second extraction	Third extraction	First extraction	Second extraction	Third extraction	First extraction	Second extraction	Third extraction
Carbonate (CO <sub>2</sub> ) (p.p.m.).....	72	75	39	168	189	90	277	172	30
Bicarbonate (HCO <sub>3</sub> ) (p.p.m.).....	201	464	354	255	610	400	396	892	678
Chloride (Cl) (p.p.m.).....	2,300	268	53	2,296	93	9	2,278	66	9
Sulfate (SO <sub>4</sub> ) (p.p.m.).....	3,964	540	107	4,218	192	41	4,239	138	56
Nitrate (NO <sub>3</sub> ) (p.p.m.).....	314	46	5	321	22	3	300	16	0
Total soluble solids (p.p.m.).....	11,134	2,257	1,006	11,702	1,750	882	11,970	1,965	1,215
pH value.....	8.4	9.3	8.6	8.6	9.4	8.4	9.0	9.0	8.2

TABLE 9  
*Constituents dissolved from soil 907 by successive extraction*

	RATIO OF SOIL TO WATER								
	1:2			1:5			1:10		
	First extraction	Second extraction	Third extraction	First extraction	Second extraction	Third extraction	First extraction	Second extraction	Third extraction
Carbonate (CO <sub>2</sub> ) (p.p.m.).....	9	28	33	67	94	63	180	180	45
Bicarbonate (HCO <sub>3</sub> ) (p.p.m.).....	294	233	211	468	327	251	640	320	358
Chloride (Cl) (p.p.m.).....	41	0	0	36	0	0	35	0	0
Sulfate (SO <sub>4</sub> ) (p.p.m.).....	264	73	40	276	57	26	289	89	32
Nitrate (NO <sub>3</sub> ) (p.p.m.).....	28	2	0	28	3	0	29	0	0
Total soluble solids (p.p.m.).....	1,161	588	508	1,705	955	750	2,225	1,175	780
pH value.....	8.0	8.5	8.3	8.4	8.9	8.2	8.8	9.0	8.2



The major portion of the chloride, sulfate and nitrate was removed from each soil by the first extraction. In fact, the quantities of these ions found in each succeeding extract was such as may reasonably be supposed to have

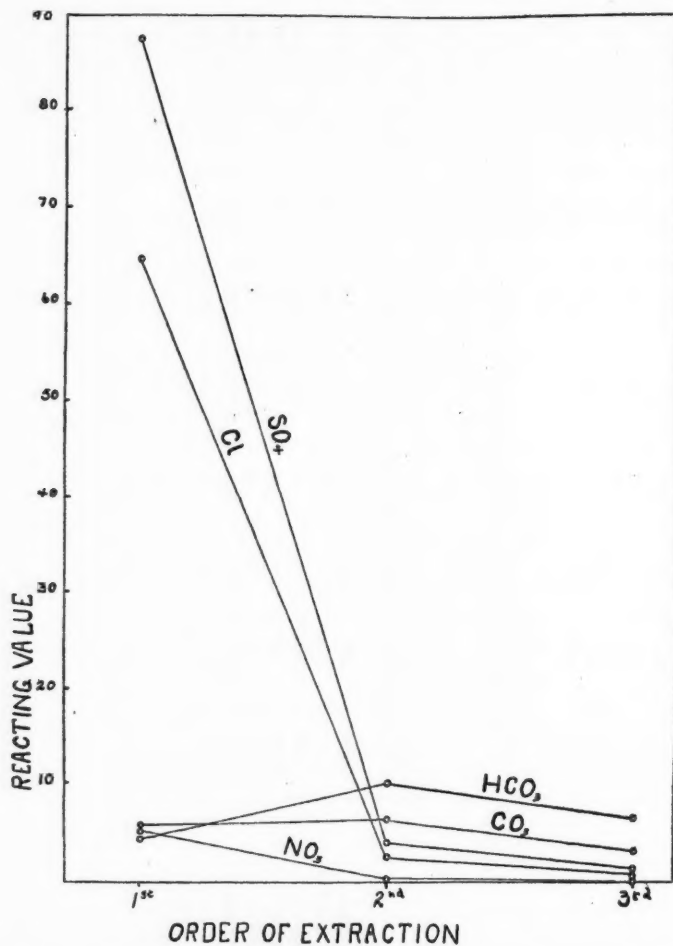


FIG. 7. CONCENTRATION OF THE VARIOUS ANIONS IN SUCCESSIVE EXTRACTS (1:5) OF SOIL 905

been derived from the adhering moisture remaining from the immediately preceding extraction.

Since the final extract from each soil still showed the presence of soluble carbonate, a sample of soil 853, which was obtained from the same locality

as soil 905, was shaken six successive times with fresh portions of water, at the ratio of 1:5. Carbonate, bicarbonate, chloride and pH values were determined in the filtrates as shown in table 11.

It will be noted that the second extract of this soil also contained greater amounts of  $\text{CO}_3$  than the first, but that, while the carbonate content of the succeeding extracts gradually decreased, small amounts still remained after the fifth extraction. The bicarbonate slowly decreased with each extraction,

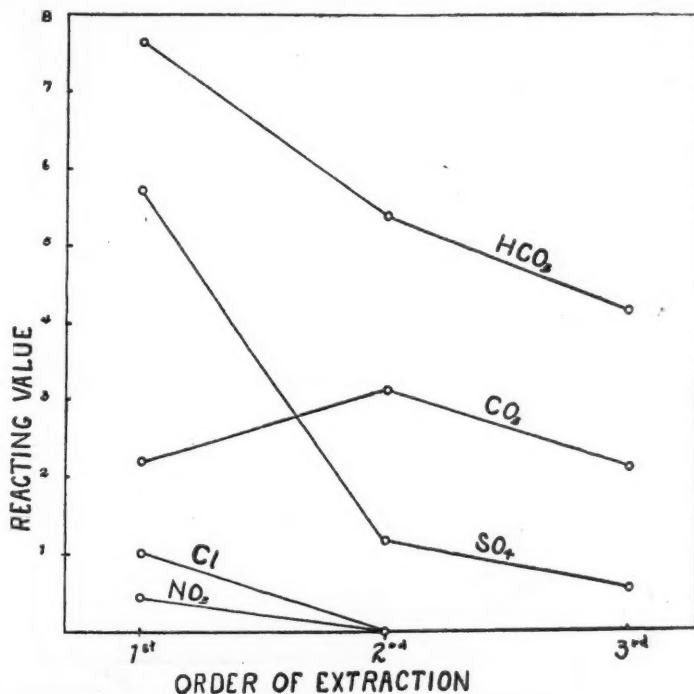


FIG. 8. CONCENTRATION OF THE VARIOUS ANIONS IN SUCCESSIVE EXTRACTS (1:5) OF SOIL 907

but considerable amounts still remained at the end of the experiment. The chloride, on the other hand, was completely removed by the second extraction.

The relative solubility of the anions in these soils becomes more apparent from a study of the data presented in tables 12, 13 and 14. In these tables are recorded the reacting values of the anions computed from the data reported in tables 8, 9 and 10. The calculations were made by multiplying the parts per million of a given ion by its reaction coefficient.<sup>3</sup>

<sup>3</sup>The reacting coefficient of an ion is the reciprocal of its weight on the atomic scale divided by its valency.

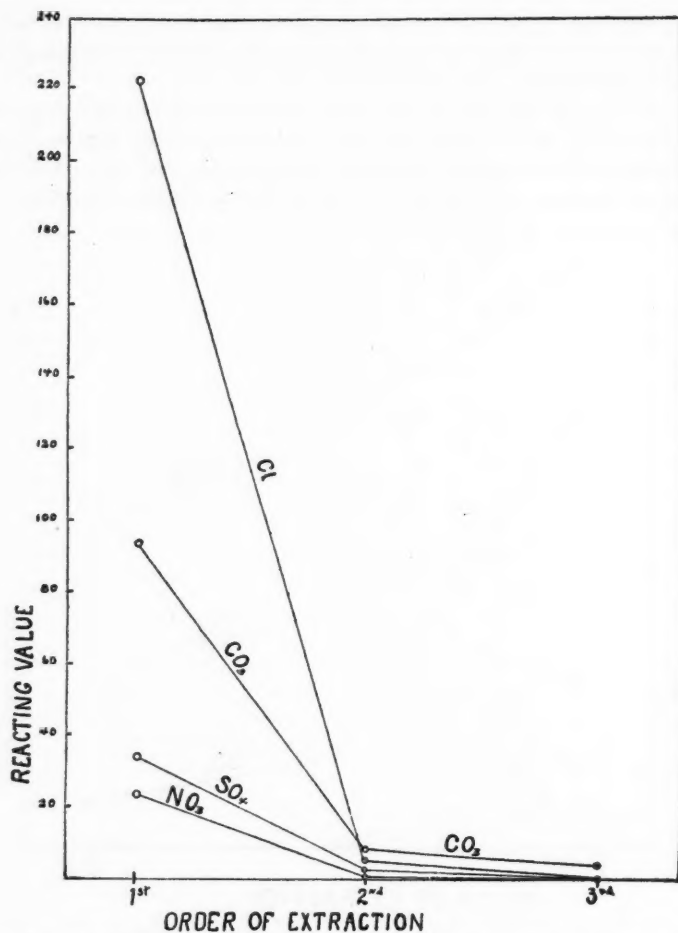


FIG. 9. CONCENTRATION OF THE VARIOUS ANIONS IN SUCCESSIVE EXTRACTS (1:5) OF SOIL 908

TABLE 11

*Results of repeated extraction with soil 853*

	ORDER OF EXTRACTION					
	First extraction	Second extraction	Third extraction	Fourth extraction	Fifth extraction	Sixth extraction
Carbonate (CO <sub>2</sub> ) (p.p.m.).....	75	112	52	30	22	15
Bicarbonate (HCO <sub>3</sub> ) (p.p.m.).....	655	625	495	472	456	442
Chloride (Cl) (p.p.m.).....	1,901	159	0	0	0	0
pH value.....	8.8	8.8	8.8	8.5	8.4	8.0



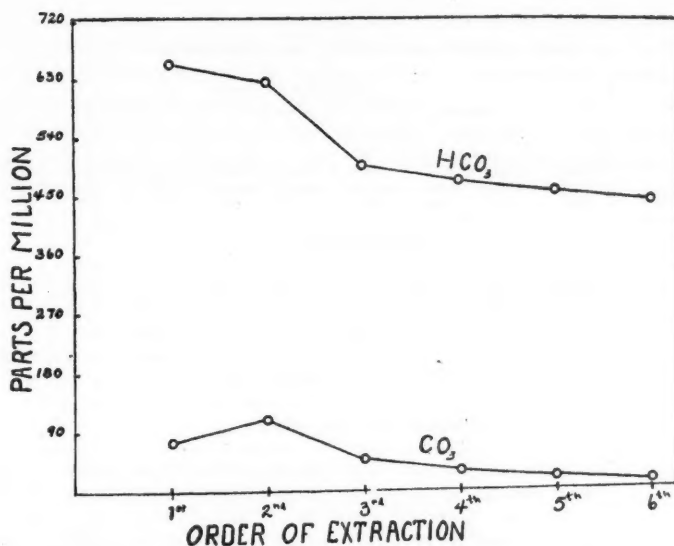


FIG. 10. AMOUNT OF CO<sub>2</sub> AND HCO<sub>3</sub> REMOVED FROM SOIL 853 BY REPEATED EXTRACTION WITH WATER

TABLE 12

*Anions dissolved from soil 905 by successive extraction*

	RATIO OF SOIL TO WATER								
	1:2			1:5			1:10		
	First extraction	Second extraction	Third extraction	First extraction	Second extraction	Third extraction	First extraction	Second extraction	Third extraction
Reacting values									
CO <sub>2</sub> .....	2.40	2.50	1.30	5.59	6.29	3.00	9.22	5.73	1.00
HCO <sub>3</sub> .....	3.29	7.61	5.80	4.18	10.00	6.56	6.49	14.63	11.12
Cl.....	64.86	7.56	1.49	64.75	2.62	0.25	64.24	1.86	0.25
SO <sub>4</sub> .....	82.45	11.23	2.22	87.73	3.99	0.85	88.17	2.87	1.16
NO <sub>3</sub> .....	5.05	0.74	0.08	5.17	0.35	0.05	4.83	0.26	0
Reacting value in percentage									
CO <sub>2</sub> .....	0.76	4.22	5.97	1.67	13.53	14.01	2.66	11.30	3.70
HCO <sub>3</sub> .....	1.04	12.84	26.63	1.25	21.50	30.62	1.88	28.86	41.09
Cl.....	20.52	12.75	6.84	19.34	5.63	1.17	18.57	3.67	0.92
SO <sub>4</sub> .....	26.08	18.94	10.19	26.20	8.58	3.97	25.49	5.66	4.29
NO <sub>3</sub> .....	1.60	1.25	0.37	1.54	0.76	0.23	1.40	0.51	0

TABLE 13

*Anions dissolved from soil 907 by successive extraction*

	RATIO OF SOIL TO WATER								
	1:2			1:5			1:10		
	First extraction	Second extraction	Third extraction	First extraction	Second extraction	Third extraction	First extraction	Second extraction	Third extraction
Reacting value									
CO <sub>3</sub> .....	0.30	0.93	1.10	2.23	3.13	2.10	5.99	5.99	1.50
HCO <sub>3</sub> .....	4.82	3.82	3.46	7.68	5.36	4.12	10.50	5.25	5.87
Cl.....	1.16	0	0	1.01	0	0	0.99	0	0
SO <sub>4</sub> .....	5.97	1.52	0.83	5.74	1.18	0.54	6.01	1.85	0.66
NO <sub>3</sub> .....	0.45	0.03	0	0.45	0.05	0	0.47	0	0
Reacting value in percentage									
CO <sub>3</sub> .....	1.23	7.38	10.20	6.52	16.10	15.53	12.50	22.88	9.34
HCO <sub>3</sub> .....	19.75	30.32	32.10	22.44	27.57	30.48	21.91	20.05	36.55
Cl.....	4.75	0	0	2.95	0	0	2.07	0	0
SO <sub>4</sub> .....	22.42	12.06	7.70	16.77	6.07	3.99	12.54	7.07	4.11
NO <sub>3</sub> .....	1.84	0.24	0	1.32	0.26	0	0.98	0	0

TABLE 14

*Anions dissolved from soil 908 by successive extraction*

	RATIO OF SOIL TO WATER									
	1:5				1:10				1:20	
	First extraction	Second extraction	Third extraction	Fourth extraction	First extraction	Second extraction	Third extraction	Fourth extraction	First extraction	Second extraction
Reacting value										
CO <sub>3</sub> .....	93.91	6.73	4.00	2.00	95.64	12.99	4.00	1.00	93.41	12.49
HCO <sub>3</sub> .....			6.05	4.74		12.76	6.62	4.76		20.01
Cl.....	222.45	5.55	0.25	0	224.22	3.50	0.25	0	229.52	4.48
SO <sub>4</sub> .....	34.26	1.84	0	0		1.91	0.42	0	35.28	0.75
NO <sub>3</sub> .....	23.94	0.42	0.21	0.14	23.46	0.29	0.18	0.11	23.89	0.11
Reacting value in percentage										
CO <sub>3</sub> .....			19.03	14.53		20.65	17.44	8.52		16.50
HCO <sub>3</sub> .....			28.78	34.45		20.29	28.86	40.54		26.44
Cl.....			1.19	0		5.56	1.09	0		5.92
SO <sub>4</sub> .....			0	0		3.07	1.83	0		0.99
NO <sub>3</sub> .....			1.00	1.02		0.46	0.78	0.94		0.15

The percentage of the different anions in a given solution also was calculated, the assumption being made that  $\text{CO}_3$ ,  $\text{HCO}_3$ ,  $\text{Cl}$ ,  $\text{SO}_4$  and  $\text{NO}_3$  were the only anions present in these solutions. As a matter of fact, small amounts of  $\text{PO}_4$  also were present and possibly  $\text{SiO}_3$  as well, but the amounts were too small to affect these calculations materially. Since the anions and cations of a solution are numerically equal, the total of either is responsible for only 50 per cent of the total reacting value of the solution.

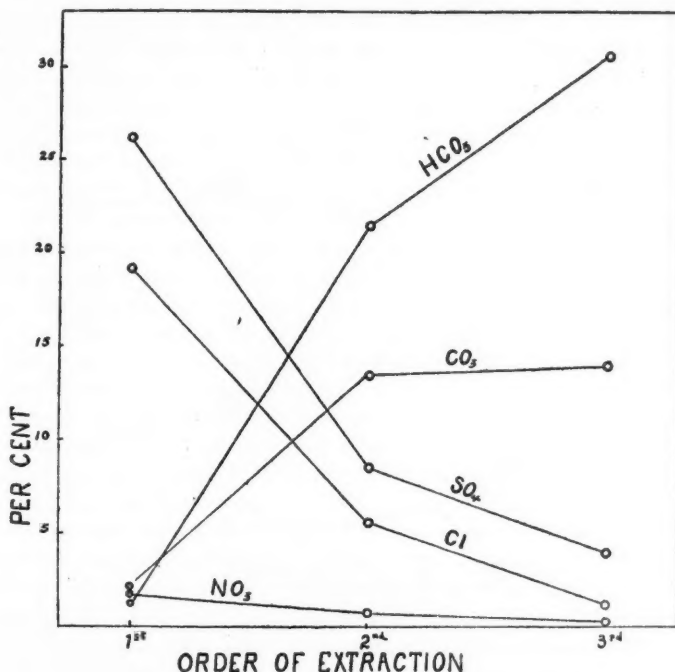


FIG. 11. REACTING VALUE OF THE ANIONS IN SUCCESSIVE EXTRACTS OF SOIL 905 EXPRESSED AS PERCENTAGE OF THE TOTAL REACTING VALUE OF THE SOLUTION

From data showing the reacting value of the different ions, together with their percentages, the true chemical nature of a solution may be readily determined. Such data afford a convenient basis for making strictly chemical comparisons between solutions of different composition and concentration; whereas their true chemical relationships may not be apparent from the ordinary analysis.<sup>4</sup>

<sup>4</sup> The chemists of the United States Geological Survey make extensive use of this principle in studying the composition of solutions (11, 13). As pointed out by Hoagland and Christie (9), agricultural chemists have not adopted it generally. Extensive use of this

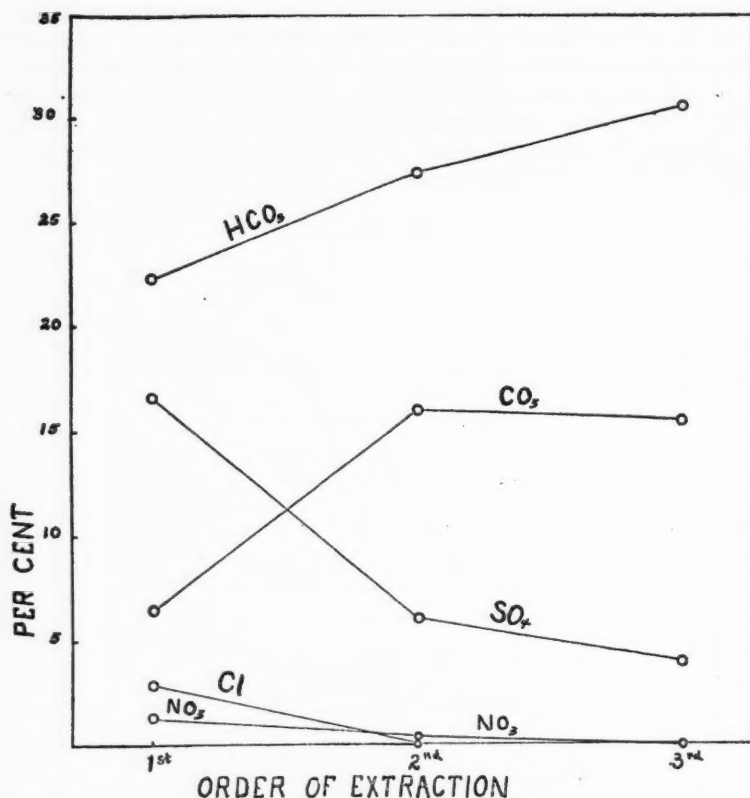


FIG. 12. REACTING VALUE OF THE ANIONS IN SUCCESSIVE EXTRACTS OF SOIL 907 EXPRESSED AS PERCENTAGE OF THE TOTAL REACTING VALUE OF THE SOLUTION

principle is made in this laboratory in studying the composition of soil extracts and irrigation waters.

It is also unfortunate that agricultural chemists should continue to report the numerical amounts of the several salts that are supposed to occur in alkali soils and irrigation water. As a matter of fact, the constituents of solutions exist in the form of ions, either in part or wholly, and not as salts. Furthermore, all of the various schemes in use for combining the different ions in mixed salt solutions are largely hypothetical and belong essentially to the realm of guess work. Moreover, Anderson and Fry (1) have shown recently that when aqueous extracts of soils are evaporated the salts crystallize out, not entirely as the simple salts of commerce, but in part as complex double salts. It would appear to be more logical, therefore, to report the ions actually determined without speculating as to their hypothetical combinations.

It will be noted that the chemical nature of the first extract of each soil was substantially different from that of subsequent extracts. The anions of the first extracts were mainly chloride (soil 908), sulfate (soil 907) or both (soil 905). The second extracts contained relatively greater percentages of carbonate and bicarbonate than the first, and finally the third and fourth extracts were composed very largely of carbonate and bicarbonate, the latter predominating.

Thus it seems quite evident that the relationship between soils and alkaline sodium salts is quite different from that between soils and neutral sodium salts. As will be shown in a subsequent paper from experiments conducted in the open field, repeated flooding accompanied by artificial drainage has thus far failed to reduce the content of sodium carbonate of one of these soils to a point sufficiently low to permit satisfactory growth of barley.

Many investigators have suggested that alkaline salts are adsorbed to a greater degree than neutral salts, but whether adsorption or the formation of chemical compounds of low solubility, as a result of reactions that take place between the alkaline salts and soil silicates or organic matter, is responsible for this fact, cannot now be stated with certainty. It seems probable that the occurrence of compounds of low solubility has more to do with the observed facts than the phenomenon of adsorption.<sup>5</sup> Whatever may be the true explanation of these data, however, they show that it is extremely difficult to remove the last trace of sodium carbonate from soils by leaching.

It seems appropriate to emphasize the fact that the difficulties encountered in removing sodium carbonate from alkali soils by leaching have usually not been recognized sufficiently, either by investigators of the alkali problem, or by those engaged in alkali reclamation. It is safe to conclude that the application of some neutralizing agent in addition to artificial flooding will be helpful in the treatment of any soil that contains black alkali, and that with certain soils the application of a neutralizing agent will probably be absolutely essential to their permanent reclamation. Hilgard proposed the use of gypsum for this purpose. In a subsequent paper we will discuss the use of various other neutralizing agents.

In a previous paper from this laboratory (10) it was shown that non-alkali soils absorb considerably more sodium from solutions of sodium carbonate or sodium hydrate than from solutions of neutral sodium salts. It was also shown that neutral sodium salts react with soils by double decomposition, forming compounds relatively high in sodium but of low solubility. In a subsequent paper it will be shown that the insoluble compounds formed by double decomposition hydrolyze in aqueous suspension yielding strongly alkaline solutions (see a recent paper by Dominicus (5)). It is possible that a portion of the alkalinity of the second and third extracts noted above may have been due to the hydrolysis of such compounds.

<sup>5</sup> See a recent paper by Bouyoucos (2).

## SUMMARY

1. The use of compressed air in filtering extracts of alkali soils was not found to affect the content of  $\text{CO}_3$  or  $\text{HCO}_3$  materially.

2. The amount of total solids dissolved by water was found to increase as the time of shaking was increased, but no consistent variation was found in the amount of any one of the anions. The conclusion is drawn that shaking for 1 hour brings about approximate equilibrium between water and the soils studied.

3. The total amounts of  $\text{CO}_3$  and  $\text{HCO}_3$  removed from two of the soils studied were found to increase as the ratio of water to soil was increased, while a third soil showed no substantial difference in the amount of  $\text{CO}_3$  dissolved.

4. Approximately equal amounts of  $\text{Cl}$  and  $\text{NO}_3$  were dissolved by every ratio of soil to water that was used, while in the case of two of the soils studied, the amount of dissolved  $\text{SO}_4$  increased somewhat as the proportion of water was increased.

5. The concentration of  $\text{OH}$  ions in the extracts of two soils was lowest where the ratio of soil to water was 1:2, and substantially increased with dilution, reaching a maximum with one soil when the ratio was 1:10 and with the other soil when the ratio was 1:40.

6. It is pointed out that the pH value of extracts or suspensions of alkali soils may be substantially higher than that of the soil solution as it occurs in the open field.

7. By extracting the same portion of soil successively with water, it was found that greater amounts of normal carbonate were dissolved by the second extraction than by the first; whereas a very large percentage of the  $\text{Cl}$ ,  $\text{SO}_4$  and  $\text{NO}_3$  were dissolved by the first extraction.

8. Solutions of substantially different chemical nature were obtained from each soil by extracting them with successive portions of water. The first extracts were composed mainly of chloride, sulfate and nitrate, while the succeeding extracts were composed of increasing percentages of carbonate or bicarbonate.

9. It seems evident that alkaline salts are either adsorbed or held in loose chemical combination by soils to a much greater degree than neutral salts.

## REFERENCES

- (1) ANDERSON, M. S., AND FRY, WILLIAM H. 1920 Solid phases obtained by the evaporation of certain soil extracts. *In* Jour. Indus. Engin. Chem., v. 12, no. 7, p. 663-669.
- (2) BOUYOUCOS, GEORGE J. 1921 The concentrations of the soil solution around the soil particles. *In* Soil Sci., v. 11, p. 131-138.
- (3) CAMERON, FRANK K., AND BRIGGS, LYMAN J. 1901 Equilibrium between carbonates and bicarbonates in aqueous solution. *In* U. S. Dept. Agr. Bur. Soils Bul. 18, p. 9-24.

- (4) CAMERON, F. K., AND PATTEN, H. E. 1906 The removal of "black alkali" by leaching. *In Jour. Amer. Chem. Soc.*, v. 28, no. 11, p. 1639-1649.
- (5) DOMINICIS, A. 1918 Terreni salsi e terreni alcalini. Contributo sperimentale sull'origine della soda nel terreno. *In Staz. Sper. Agr. Ital.*, v. 51, no. 3-6, p. 103-161.
- (6) DORSEY, CLARENCE, W. 1906 Alkali soils of the United States. A review of the literature and summary of present information. U. S. Dept. Agr. Bur. Soils Bul. 35.
- (7) HARE, R. F. 1915 A review and discussion of some of the methods for the determination of alkali in soils. *In N. M. Agr. Exp. Sta. Bul.* 95, p. 7-16.
- (8) HOAGLAND, D. R. 1917 The effect of hydrogen and hydroxyl-ion concentration on the growth of barley seedlings. *In Soil Sci.*, v. 3, no. 6, p. 547-560.
- (9) HOAGLAND, D. R., AND CHRISTIE, A. W. 1919 The effect of several types of irrigation water on the pH value and freezing-point depression of various types of soils. *In Univ. Cal. Pub. Agr. Sci.*, v. 4, no. 6, p. 141-158.
- (10) KELLEY, W. P., AND CUMMINS, A. B. 1921 Chemical effect of salts on soils. *In Soil Sci.*, v. 11, no. 2, p. 139-159.
- (11) PALMER, CHASE 1911 The geochemical interpretation of water analyses. U. S. Geol. Survey Bul. 479.
- (12) PITTMAN, D. W. 1919 A study of methods of determining soil alkali. Utah Agr. Exp. Sta. Bul. 170.
- (13) ROGERS, G. SHEERBURNE 1917 Chemical relations of the oil-field waters in San Joaquin Valley, California. U. S. Geol. Survey Bul. 653.
- (14) VINSON, A. E., AND CATLIN, C. N. 1913 Study of methods used in alkali determinations. *In Ariz. Agr. Exp. Sta. 24th Ann. Rpt.*, p. 274-277.
- (15) WEIR, WALTER W. 1916 Preliminary report on Kearney Vineyard experimental drain. Cal. Agr. Exp. Sta. Bul. 273.